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HANDBOOK OF METALLURGY

HANDBOOK
OF
METALLURGY

BY

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VOL. II

ZINC—CADMIUM—MERCURY—BISMUTH—TIN—ANTIMONY
ARSENIC—NICKEL—COBALT—PLATINUM—ALUMINIUM

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HANDBOOK OF METALLURGY

METALLURGY.

ZINC

PHYSICAL PROPERTIES

ZINC possesses a white colour with a bluish grey tinge, and a high lustre on a freshly fractured surface. It crystallises in the cubical system. The nature of the fracture depends upon the temperature at which the metal was poured, and is independent of the subsequent rate of cooling; it is coarsely lamellar when the fluid metal was heated to redness before pouring, but fine grained when it is cast at its melting point.

The specific gravity of unrolled zinc is 6·861 according to Brisson, 6·9154 according to Karsten, 7·149 according to Matthiessen. Zinc cast at its melting point and slowly cooled has a specific gravity of 7·145 according to Bolley, and of 7·128 according to Rammelsberg; whilst when cast at a red heat and cooled slowly, it is 7·120 according to the former, and 7·101 according to the latter observer; if cast at its melting point and cooled rapidly, it has, according to the former, a specific gravity of 7·158, and, according to the latter, of 7·147; whilst the respective results obtained from zinc, poured at a red heat and cooled rapidly, are 7·109 and 7·037.[1] Its specific gravity is raised from 7·2 to 7·3 by rolling.

At ordinary temperatures, zinc is so brittle that ingots and slabs are readily broken; between 100° and 150° C. it becomes so malleable that it can be rolled into thin sheets and drawn into wire; at 200° C. it again becomes so brittle that it can be pounded into powder.

Berthier found that a wire 0·002 m. in diameter broke with a load of 12 kilos; according to Karmarsch the tenacity of cast zinc is 197·5 kilos, and that of sheets and wire between 1315 and 1560 kilos per square centimetre (2,809 lbs., 18,703 lbs. and 22,188 lbs. per square inch respectively).

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[1] Stolzel, *Metallurgie*, Brunswick, 1874, p. 752.

According to Regnault, the specific heat of zinc is 0·09555 for temperatures between 0° and 100° C.

Zinc expands by $\frac{1}{340}$ of its length when heated from 0° to 100° C. According to Calvert and Johnson, the coefficient of linear expansion of hammered zinc is 0·002193.

The conductivity of zinc, silver being taken at 1000, is 281 according to Wiedemann and Franz; that of cast zinc is between 608 and 628, and that of rolled zinc 641, according to Calvert and Johnson.

The electric conductivity of zinc, silver being taken at 100, is 24·06 according to Becquerell, 27·39 according to Matthiessen, and 29·90 according to Weiller.[1]

Zinc melts at 412° C. according to Daniell, and at 434° according to Person. It volatilises at bright redness, its boiling point being 891° C. according to Becquerell, 1040° according to Deville and Troost, and 929·6° according to Violle; silver (melting about 954° C.) does not melt in zinc vapour. Zinc vapour can be condensed to fluid zinc by cooling; the more diluted it is with air, the more difficult is this vapour to condense. When the temperature of the vapour falls below the melting point of zinc, it solidifies in the form of powder, forming what is known as *zinc fume*. According to Lynen,[2] the zinc vapour produced in the extraction of zinc from its ores condenses between 415° and 550° C. According to Hempel,[3] zinc vapour, formed by the reduction of zinc white in the blast furnace, was not condensed from the gases accompanying it until the temperature had fallen below 470°.

When heated in the air to its boiling point, zinc burns with bright greenish and bluish white flame to zinc oxide.

Commercial zinc is generally rendered impure by the presence of lead, cadmium and iron, and in many cases also of small quantities of tin, copper, arsenic, sulphur, carbon and chlorine.

The effect of the impurities contained in the zinc upon the properties of the latter has been investigated by Karsten[4] and by Eliot and Storer.[5]

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[1] *Journ. Franklin Inst.*, April, 1892, p. 263.

[2] Zinc distillation furnace with common condensing chamber. London, 1893.

[3] *Berg. u. Hütt. Ztg.*, 1893, No. 41, 42.

[4] Karsten's *Archiv*, 1842, vol. xvi., p. 597.

[5] "On the impurities of commercial zinc with reference to the residue insoluble in dilute acid, to sulphur and to arsenic." *Memoirs Am. Acad. Arts and Sciences.* New series, vol. viii., 1860.

Lead is present in most varieties of commercial zinc. Karsten found the proportion in Silesian zinc to vary between 0·24 and 2·36 per cent. Eliot and Storer found only 0·079 per cent. of lead in New Jersey zinc, and none at all in zinc from Pennsylvania reduced from the silicate.

The amount of lead that zinc can take up varies with the temperature, being greater the higher the temperature. According to the most recent researches on this subject, of Roessler and Edelmann, zinc takes up 1·7 per cent. of lead at its melting point and 5·6 per cent. at 650° C. If more lead is present than corresponds to the temperature of the metal, the excess separates out in the liquid state.

A considerable proportion of lead makes zinc tender; with 1½ per cent. of lead, it can still be rolled without cracking, but becomes softer and more tender. It can even be rolled with 3 per cent. of lead, but shows the above characteristics more markedly. Before zinc is rolled, lead is removed from it as completely as possible by remelting the metal and allowing it to settle.

Cadmium occurs in most varieties of zinc, because this metal is present in most zinc ores. As cadmium is considerably more volatile than zinc, it is only to be found in very small amounts in commercial zinc. According to some experiments of Mentzel in 1829, at the Lydognia Works in Upper Silesia, cadmium would seem to diminish the softness of zinc as soon as it is present in certain proportions. In the small amounts in which it exists in commercial zinc, it has no injurious effects upon the properties of the latter.

Iron may be contained in zinc to the extent of several per cent., but rarely exceeds 0·2 per cent. The highest proportion of iron found by Karsten was 0·24 per cent., and by Percy[1] 1·64 per cent. Eliot and Storer found 0·21 per cent. of iron in New Jersey zinc, and 0·05 to 0·07 per cent. in sheet zinc from Berlin. Oudemans found in a difficultly fusible substance with white, lustrous, hackly fracture, which collected in iron kettles in which zinc had been kept molten for many weeks, 4·6 per cent. of iron. In small quantities—up to 0·2 per cent. according to Karsten—iron does not affect the properties of zinc; in larger proportion, however, it renders the zinc hard and unfit for rolling.

Tin has only been found by Eliot and Storer in American zinc from New Jersey and English zinc made by Vivian and Co., of Swansea. According to Karsten, 1 per cent. of tin renders zinc brittle at those temperatures at which it would otherwise be malleable.

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[1] *Metallurgy. First Division*, 1861, page 590.

Copper was only found by Eliot and Storer in New Jersey zinc. Karsten found that ½ per cent. of copper makes zinc harder and brittle, so that it showed ragged edges on rolling, and could not be rolled without cracking.

Arsenic occurs in small quantities in many varieties of zinc; it has not been observed to have any effect upon the properties of the latter. Nothing is known as to the influence of larger quantities of arsenic.

Sulphur could not be detected by Karsten in any of the numerous samples of zinc examined by him. On the other hand, Eliot and Storer, as also Alfred Taylor, found small amounts of sulphur in a large number of varieties of zinc. No investigations have been made as to the effect of sulphur on the properties of zinc; the small amounts found in zinc seem not to affect the latter.

Carbon was found by Jacquelain in very small proportion (0·003 per cent.) in one variety of zinc; Rodwell[1] found sulphate of lead, carbon and a trace of iron in the black residue that remains when commercial zinc is dissolved in sulphuric acid. It cannot be determined whether this carbon is dissolved in the zinc or mechanically mixed with it. Such a small proportion of carbon seems not to affect the zinc in the least, whilst nothing is known as to its action in larger quantities.

Chlorine has been detected by C. Künzel in a Belgian zinc that was prepared from the dross of galvanised iron, in quantities of 0·2 to 0·3 per cent.; this zinc, which contained only traces of lead and iron, could not be rolled.

CHEMICAL PROPERTIES

Zinc is not affected in dry air at ordinary temperatures; in damp air in the presence of carbon dioxide, it becomes coated with a layer of hydrated basic zinc carbonate, which layer is sufficiently dense to protect the metal beneath it from any further atmospheric action.

The massive metal is not attacked at ordinary temperatures by water free from air, but in the presence of air and carbon dioxide it is changed into the above-named basic carbonate.

When zinc is heated in the air, it takes fire at a temperature approaching redness (at 505°C. according to Daniell), and burns with a luminous greenish and bluish white flame to zinc oxide, which in part floats as an incrustation upon the surface of the molten metal, and in part appears as a snow-white flocculent body (*lana philosophica*).

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[1] *Chem. News*, January, 1861, No. 57.

Zinc decomposes water at a red heat, and is transformed into zinc oxide with the evolution of hydrogen. Zinc in a very fine state of division exerts a very feeble decomposing action upon water even at ordinary temperatures; this action is favoured by the presence of acids and alkalis.

Zinc is soluble in most acids. In dilute sulphuric and hydrochloric acids it dissolves with the evolution of hydrogen, the rate of solution being more or less rapid according to the molecular condition and purity of the metal. According to Bolley, zinc melted at a low temperature dissolves more slowly than when melted at a red heat.

Chemically pure zinc dissolves more slowly than metal contaminated with small amounts of impurities (Fe, Cu, Pb). According to l'Hôte,[1] pure zinc is not attacked by dilute sulphuric acid. The difficult solubility of chemically pure zinc in acids is, according to Werren,[2] due to the fact that the metal becomes surrounded by a film of hydrogen the moment it is dipped into the acid; on boiling, this film is torn, and the zinc dissolves. Zinc dissolves readily in cold nitric acid, because the latter oxidises the hydrogen evolved. The solubility of zinc in sulphuric acid is promoted by the addition of chromic acid and of hydrogen peroxide. Impure zinc dissolves readily in acids, because the hydrogen is evolved, not from the zinc, but from the more electronegative foreign metals.

Zinc is converted by carbon dioxide into zinc oxide at a red heat, carbon monoxide being formed.

Aqueous solutions of the alkalies attack zinc with the evolution of hydrogen, but much more slowly than do acids. The action is more energetic when the zinc is in contact with iron or platinum so as to form a galvanic couple. Zinc is thus easily dissolved in potash lye when contained in an iron vessel.

Zinc precipitates all the malleable heavy metals except iron and nickel from their solutions in the metallic state. Conversely it is not precipitated as metal from its solutions by any metal that is permanent in the air at ordinary temperatures.

Sulphur combines with zinc at a red heat, producing zinc sulphide; the combination is, however, imperfect, because the zinc, even when in fine powder and intimately mixed with powdered sulphur, is protected by the superficial layer of the infusible sulphide thus formed. Zinc can be converted completely into sulphide by rapid heating with cinnabar, as also by fusion with potassic sulphide.

By fusion with litharge, zinc is converted into oxide, whilst the oxide of lead is reduced to metal.

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[1] *Comptes Rendus*, 1885, 101, p. 1153.

[2] *Ber. d. Chem. Ges.*, 1891, 24, p. 1785.

By fusion with alkaline carbonates, zinc is converted into oxide with the evolution of carbon monoxide. When it is similarly treated with alkaline sulphates, zinc sulphate together with zinc oxide are formed, sulphur dioxide being evolved. Zinc unites with phosphorus at a red heat in various proportions to form phosphides of zinc.

Zinc unites with arsenic in all proportions at a moderate temperature, alloys of the two metals being produced. The more arsenic it contains, the more difficultly fusible does the zinc become; alloys containing large proportions of arsenic are absolutely infusible.

Zinc forms alloys with a large number of metals.

CHEMICAL REACTIONS OF ZINC COMPOUNDS THAT ARE OF IMPORTANCE IN THE EXTRACTION OF THE METAL

ZINC OXIDE (ZnO)

Zinc forms only one compound with oxygen, namely zinc oxide; this occurs in nature as zincite. Artificially it is prepared by burning zinc, by heating finely divided zinc with nitre, potassic chlorate or arsenic acid, by igniting zinc carbonate, hydrate, sulphate or nitrate, and by the oxidising roasting of zinc sulphide.

It forms a white or pale yellow powder, which becomes lemon-yellow on heating, but regains its white colour on cooling.

Zinc oxide is infusible by itself, and is unaffected at temperatures that are not excessive, but is volatile at a strong white heat. According to experiments of Stahlschmidt,[1] pure zinc oxide is perceptibly volatile even at the melting point of silver; at the melting point of copper its volatility is more marked (15 per cent.). At a white heat it volatilises rapidly.

Zinc oxide is insoluble in pure water. Acids dissolve it readily, as also do solutions of caustic potash and soda, ammonia and ammonic carbonate. With sulphurous acid it forms zinc sulphite.

Although zinc oxide is a strong base, it nevertheless combines also with other bases (with the alkalies and with alumina). It combines with water to form zinc hydrate, which is reconverted into oxide on heating.

It is reduced to metal by carbon and carbon monoxide at a bright red heat. According to Hempel's[2] experiments, reduction commences at a temperature below the boiling point of zinc, and is complete at a temperature above it, between bright redness and a white heat.

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[1] *Berg. u. Hutt. Ztg.*, 1875, p. 69.

[2] *Ibid.*, 1893, Nos. 41 and 42.

When reduced by means of carbon, carbon monoxide is formed; when reduced by carbon monoxide, carbon dioxide is evolved. The former gas is without action on zinc at any temperature, the latter oxidises it at a red heat. The quantity of zinc oxidised in any given case by a mixture of carbon monoxide and dioxide would seem to depend on the one hand upon the ratio in which these gases are present, and on the other hand upon the temperature. (See the reduction of zinc oxide by hydrogen.)

When zinc oxide is heated with a sufficient quantity of carbon to its reducing point, zinc is first reduced by the carbon. The carbon monoxide thus formed itself reduces the oxide of zinc, becoming thereby converted into carbon dioxide. The latter has no opportunity of oxidising the zinc, because it is straightway reduced to carbon monoxide again by the red hot carbon. As long, therefore, as a sufficiency of red hot carbon is present, zinc and carbon monoxide alone are produced. Any small amount of oxide produced by the oxidation of zinc is reduced again to metal by the carbon and carbon monoxide. These reactions would seem also to take place in the production of zinc from zinc oxide on the large scale. As carbon monoxide thus acts as a reducing agent, a very intimate mixture of zinc oxide with the carbon, or a very fine state of division of these bodies, is unnecessary.

Zinc oxide produced by the dead roasting of zinc blende is more difficultly reducible than that formed by the calcination of the carbonate.

Hydrogen reduces zinc oxide to zinc at a red heat; the water vapour thus produced oxidises the zinc again to a greater or less extent. According to the experiments of Deville[1] and Dick,[2] zinc chiefly is obtained when a considerable quantity of hydrogen is passed in a rapid stream over the red hot oxide, whilst almost all the zinc is again oxidised when a slow current of hydrogen is passed over the oxide. The oxidising action of the water vapour upon the zinc would seem to depend both on the ratio of the water vapour to the hydrogen and on the temperature. Deville is of the opinion that temperature is the essential factor, a rapid current of hydrogen causing a fall in temperature that is not produced by a slow one; at this lower temperature water vapour cannot exert the oxidising action that it does at the higher. Further experiments are needed to decide whether this view is or is not the correct one.

Sulphur attacks zinc oxide when heated, zinc sulphide and sulphur dioxide being produced.

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[1] *Ann. d. Chim. et Phys.* (3) vol. xliii., p. 479.

[2] Percy, *Op. cit.* p. 535.

At high temperatures iron[1] reduces zinc oxide to metal.

Zinc oxide unites with silica at a white heat to form silicates. Percy[2] found that the bisilicate could not be made to fuse at the highest white heat, whilst the monosilicates and the lower silicates fused at this temperature to more or less translucent slags of whitish- to greenish-yellow colour. According to Stelzner and Schulze,[3] incrustations of silicates of zinc often form on the exterior of zinc-distillation muffles, which are permeated by zinc vapours. In one case, one of these silicates contained: ZnO, 56·11 per cent.; Fe_2O_3, 0·81 per cent.; SiO_2, 42·77 per cent. These observers found in the blue portions of the muffle walls a zinc-alumina spinel, tridymite, and a glass consisting of silicate of zinc.

Zinc oxide combines with alumina at high temperatures to form aluminates. By heating an intimate mixture of zinc oxide and anhydrous alumina in the equivalent proportions of 1 : 6, Percy[4] obtained a grey sintered stony mass that scratched flint glass. In the blue portions of the walls of vessels used for distilling zinc, Wohlfahrt, Stelzner and Schulze[5] found a blue zinc-alumina spinel, in which a small portion of zinc oxide was replaced by ferrous oxide, its formula being $ZnO\ Al_2O_3$, and its composition—

ZnO	42·60
FeO	1·12
Al_2O_3	55·61
	99 33

When heated with eight times its weight of oxide of lead, zinc oxide melts to a limpid pale yellow fluid;[6] when from six to seven times its weight is taken, the mass becomes pasty; on further diminishing the proportion of oxide of lead, difficultly fusible and ultimately infusible.

The behaviour of zinc sulphide with zinc oxide will be found under Zinc Sulphide.

Zinc oxide melts with fixed alkaline carbonates to fluid, colourless transparent substances as long as its weight does not exceed one-fifth of the whole.[7]

Zinc oxide is dissolved as chloride of zinc by a solution of ferric chloride, an equivalent quantity of iron being precipitated as hydrate.

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[1] Percy. *Op. cit.* p. 536.

[2] Percy. *Op. cit.* p. 536.

[3] *Jahrb. f. Berg. u. Hüttenwesen im Königreich Sachsen*, 1881. *Berg. u. Hütt. Ztg.*, 1886, p. 150.

[4] *Op. cit.* p. 539.

[5] *Loc. cit.*

[6] Berthier, vol. i., p. 515.

[7] Berthier, vol. ii., p. 567.

ZINC SULPHIDE (ZnS)

Zinc sulphide occurs in nature as zinc blende. This compound can be produced artificially in both the wet and the dry way. In the latter it is obtained by heating zinc oxide with sulphur, or in a stream of sulphuretted hydrogen, by heating zinc filings with cinnabar, by heating zinc filings or granulated zinc with alkaline polysulphides, and by heating zinc sulphate and carbon to a white heat. As already stated, it is only partially formed when zinc and sulphur are heated together, but has been produced by repeated compression of a mixture of these two substances.

In the wet way it is produced as an amorphous white powder by precipitating zinc solutions with ammonic sulphide or sulphuretted hydrogen.

Sulphide of zinc is infusible; according to experiments of Percy[1] it seems to be perceptibly volatile at high temperatures.

It can be melted to a certain extent with other metallic sulphides, forming a regulus, which it tends to render difficultly fusible. It also melts to some extent with slags, rendering these difficultly fusible, unless considerable quantities of ferrous oxide are present in them.

When pulverulent zinc sulphide is heated to redness in the air, zinc oxide and sulphate form, sulphur dioxide being given off. When the temperature rises to cherry redness, zinc sulphate is decomposed into sulphur trioxide, sulphur dioxide, oxygen and basic zinc sulphate; when it rises still further to a full red heat approaching whiteness, the last-named salt is decomposed into zinc oxide, sulphur trioxide, sulphur dioxide and oxygen.

When zinc sulphide is heated in water vapour, zinc oxide and sulphuretted hydrogen are formed; this decomposition is, however, imperfect, and requires a temperature up to white heat.

When zinc sulphide is heated with carbon or in carbon-lined crucibles it volatilises completely according to Percy,[2] or only leaves behind, if it was ferriferous, a residue of ferrous sulphide free from zinc. It is not stated whether the zinc sulphide volatilised unchanged or whether it was reduced by the carbon (with the formation of carbon disulphide), in which case metallic zinc must have been produced. These experiments certainly need further elucidation.

Zinc sulphide heated with carbon and lime produces metallic zinc, calcium sulphide being formed;[3] the decomposition is, however, incomplete, and is said by Berthier to depend on the temperature.

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[1] *Op. cit.* p. 540.

[2] *Op. cit.* p. 543.

[3] Berthier, *Tr. d. Essais*, vol. ii., p. 570.

Iron decomposes zinc sulphide at a bright red heat, with the formation of ferrous sulphide and zinc vapour; it is probable that a small amount of zinc sulphide will, however, unite with the iron sulphide, and thus escape decomposition.

According to Percy,[1] tin only decomposes zinc sulphide imperfectly at bright redness.

Antimony appears not to decompose zinc sulphide, according to Percy's experiments,[2] and lead only very imperfectly.[3] Copper decomposes it, according to the same authority,[4] at a white heat with the formation of a copper regulus.

Hydrogen has no effect upon zinc sulphide, according to Berthier.[5] According to Morse,[6] zinc sulphide can be apparently sublimed in a current of hydrogen. This circumstance is said to be caused by the reduction of the sulphide in the presence of excess of hydrogen with the formation of sulphuretted hydrogen, whilst at a lower temperature the volatilised metal takes the sulphur up again from the latter gas.

According to Berthier, zinc oxide and zinc sulphide, when heated together in any proportions, form fusible oxysulphides

Percy[7] deduces, from some rather imperfect experiments, that sulphide and oxide of zinc mutually decompose each other at high temperatures, like sulphide and oxide of copper. With suitable proportions it would accordingly be possible to reduce the whole of the zinc with the formation of sulphur dioxide, whilst any excess of sulphide or oxide would remain in the residue. If Percy's deductions are correct, considerable quantities of zinc might thus be won; but his experiments require confirmation.

Zinc sulphide and cuprous oxide appear, from similarly incomplete experiments of Percy's,[8] to decompose each other, a button looking like copper, and a regulus being produced.

Zinc sulphide and litharge, heated together in suitable proportions, decompose each other, according to Berthier,[9] the products being lead, zinc oxide and sulphur dioxide. If the zinc oxide thus formed is to form a liquid mass with the excess of lead oxide, there must be 25 times as much lead as zinc oxide present; in these proportions a resin-like glassy slag is obtained. By heating a mixture of 24·08 grms. of blende with 55·78 grms. of litharge, Berthier obtained 29·2 grms. of blackish-grey hard lead, with 1·8 per cent. of sulphur and 0·8 per cent. of zinc. Above the lead was a layer consisting of sulphides and oxides of lead and zinc together with sulphur.

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[1] *Op. cit.* p. 543.

[2] *Op. cit.* p. 543.

[3] *Op. cit.* p. 543.

[4] *Op. cit* p. 544.

[5] *Annales des Mines* (3), vol xi., p. 46.

[6] *Chem Ztg*, 1889, p 179.

[7] *Op. cit* p. 542.

[8] *Op cit.* p. 544.

[9] *Op. cit*, vol. i., p. 403

Carbon dioxide has no action upon zinc sulphide, even at a red heat.

When zinc sulphide and nitre are heated together, zinc oxide and potassium sulphate are produced.

By fusing alkaline carbonates with zinc sulphide at a red heat, mixtures of zinc oxide, zinc sulphate and alkaline sulphides are obtained.

Zinc sulphide and lime only decompose each other, according to Berthier,[1] in the presence of carbon. By heating 6·32 grms. calcium carbonate and 6·03 grms. zinc sulphide to a very high temperature, five-sixths of the zinc was volatilised, whilst the residue, weighing 4·6 grms., contained but little sulphide of zinc. Percy[2] heated up to a white heat 35 grms. of blende with 35 grms. of lime, without carbon, in a lime crucible placed inside a graphite pot and separated from it by a layer of lime, and obtained a pale brown, porous, imperfectly fused mass, weighing 27 grms; the latter yielded a little sulphide (calcium polysulphide) to boiling water, and dissolved in hydrochloric acid with the evolution of sulphuretted hydrogen, the resulting solution containing zinc. The above experiment does not, however, prove whether the decomposition of sulphide and oxide of zinc is in any degree a complete one. Attempts have been made to utilise the interaction of zinc sulphide, zinc oxide and carbon for the production of zinc on the large scale, but have been given up, on account of the imperfect reduction of the zinc compounds.

ZINC SILICATE

This compound occurs naturally anhydrous as willemite (Zn_2SiO_4), and hydrated as hemimorphite ($Zn_2SiO_4 + H_2O$). As already stated, it is obtained artificially by heating zinc oxide and silica to a white heat.

By heating to whiteness with carbon, the zinc of both the natural and the artificial silicate can be completely reduced to metal. According to experiments of Percy,[3] complete reduction is also obtained when the finely powdered silicate is heated without any admixture of carbon in carbon-lined crucibles, but the reduction is imperfect when the silicate is treated in fragments of the size of peas in such crucibles.

When zinc silicate is strongly heated with carbon and lime, the zinc is also completely reduced.

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[1] *Op. cit.* vol. ii., p. 570.

[2] *Op. cit.* p. 546.

[3] *Op. cit.* p. 537.

ZINC CARBONATE ($ZnCO_3$)

This compound occurs in nature as smithsonite, and in the form of a basic hydrated salt as hydrozincite ($ZnCO_3 + 2ZnH_2O_2$). It is produced artificially as a basic hydrate by driving off the ammonia from a solution of zinc oxide in ammonium carbonate.

By heating zinc carbonate to redness, the carbon dioxide is expelled, zinc oxide remaining behind; when heated with carbon or carbon monoxide up to the reduction temperature of zinc oxide, metallic zinc is produced.

ZINC SULPHATE ($ZnSO_4$)

This salt crystallises as $ZnSO_4 + 7H_2O$, in which hydrated condition it occurs naturally as goslarite. It is prepared artificially by dissolving zinc, zinc oxide or zinc carbonate in sulphuric acid, as also by roasting zinc sulphide with access of air at the lowest possible temperature.

On heating, zinc sulphate is converted into zinc oxide, the sulphur trioxide being evolved partly as such and partly splitting into sulphur dioxide and oxygen.

Carbon decomposes zinc sulphate on heating; at a red heat a mixture of carbon and zinc oxide is left behind, sulphur dioxide and carbon dioxide being evolved; at a higher temperature the carbon reduces the zinc oxide to metal. If on the other hand a mixture of zinc sulphate and carbon is heated sharply to whiteness, zinc sulphide and carbon monoxide are formed.

A solution of zinc sulphate is decomposed by a galvanic current, zinc going to the cathode, and the acid radical to the anode.

ZINC CHLORIDE ($ZnCl_2$)

This salt is produced by dissolving zinc, its oxide or its carbonate in hydrochloric acid, by the action of ferric chloride on zinc oxide, and by the chloridising roasting of zinc sulphide. The salt is volatile at a red heat. Its solutions are decomposed by the galvanic current, zinc separating at the cathode and chlorine at the anode.

ALLOYS OF ZINC

Zinc alloys with many metals, for example, gold, silver, copper, lead, nickel, tin, antimony.

It has greater affinity for silver than lead has; silver can therefore be extracted from molten argentiferous lead by the aid of zinc. A mixture of various alloys of lead, zinc and silver is thus produced, out of which the greater part of the lead may be liquated. If both the lead and the zinc are free from copper, whilst a small proportion of aluminium is added to the zinc, a fairly rich zinc-silver alloy can be obtained. From the triple lead-silver-zinc alloy the zinc may be removed by distillation, by oxidation, by slagging, and by treatment with dilute sulphuric acid; the latter method can also be used for zinc-silver alloys, as may also distillation and electrolysis.

Zinc is therefore used for enriching poor argentiferous lead and for collecting the silver in alloys of either lead, zinc and silver, or of zinc and silver.

By heating zinc alloys to the boiling point of zinc, the latter may be vaporised and obtained by condensing the vapours.

If water vapour is passed into a red-hot, molten lead-silver-zinc or lead-zinc alloy, it is decomposed by the zinc present, hydrogen being evolved and zinc oxide formed, whilst silver-lead or lead, as the case may be, remains behind.

By fusing the above zinc alloys with lead oxide, the zinc may be separated out as oxide.

By fusing lead-zinc alloys or lead-silver-zinc alloys with common salt, the zinc is converted into chloride, the other metals remaining unchanged.

By the aid of a suitable electrolyte, with a proper strength of current, zinc may be electrolytically dissolved from its alloys and thrown down at the cathode.

ZINC ORES

The most important ores of zinc are zinc blende, calamine and hemimorphite. The other ores, hydrozincite, zincite and franklinite, are of far less metallurgical importance, on account of their scarcity.

ZINC BLENDE OR SPHALERITE (ZnS)

Zinc blende forms at present the main source of zinc production. It rarely consists of pure sulphide of zinc, but generally contains sulphide of iron, together with smaller quantities of the sulphides of cadmium and silver isomorphously mixed with it. Pure zinc blende contains 67 per cent. of zinc. The ratio of iron present varies generally from 1 per cent. to 18 per cent.; that of cadmium may go up to 3 per cent.

Zinc blende is found in most countries, In Europe the chief localities are Germany (the Harz, the Erzgebirge, Silesia, Westphalia), the Rhine district (Hessen-Nassau and Baden), Austro-Hungary

(Carinthia, Hungary, Tyrol and Bohemia), Italy (Sardinia, Lombardy and Piedmont), Belgium (Corphalie and Engis), England (Wales, Cornwall, Cumberland,. Isle of Man, Anglesea, Denbighshire and Shropshire), France, Spain (Santander), Sweden (Ammeberg and Copparberg), Russia (Allagin and the Donetz basin), Greece. In Africa, Algeria; in Australia, New South Wales (Broken Hill); in Asia, Siberia (Altai); in America, the United States (New Jersey, Missouri, Pennsylvania, Wisconsin and Colorado), Mexico and South America (Huanchaca).

Blende is frequently accompanied by pyrites, chalcocite, galena and various arsenides and antimonides, as also by quartz, calcite, dolomite, siderite, and in many instances by mica, chlorite and hornblende.

CALAMINE OR ZINC SPAR ($ZnCO_3$)

This ore was formerly the chief source of zinc. At present a great number of the true deposits of calamine are exhausted, whilst others that carried calamine in the shallower portions have passed into blende in depth. The quantity of this ore that is treated has hence fallen off considerably.

Calamine is rarely pure carbonate of zinc, but contains as a rule the isomorphous carbonates of cadmium, iron, manganese, calcium and magnesium. If quite pure, it would contain 52 per cent. of zinc, whilst the impure ore containing other carbonates may have under 40 per cent. of zinc; the proportion of cadmium may go up to several per cents.

Calamine occurs in Europe, in Germany (Upper Silesia, Rhine districts, Westphalia and Baden), Austro-Hungary (Carinthia), Belgium, Russia (Poland), Greece (Laurium), Italy (Sardinia), Spain (Santander, Granada, Carthagena, Almeria and Castillon); in America, in the United States (Missouri, Virginia, New Jersey, Tennessee, Arkansas and Pennsylvania); in Africa, in Algeria.

This ore is generally intermixed with clay, brown iron ore, red hæmatite, galena, dolomite and calcite; what is known as white calamine contains clay as its chief impurity, whilst red calamine contains anhydrous and hydrated oxides of iron and oxide of manganese.

ELECTRIC CALAMINE, HEMIMORPHITE OR ZINC SILICATE ($Zn_2SiO_4 + H_2O$)

This ore contains 53·7 per cent. of zinc when pure, and is often intermixed with the last-named. It occurs in considerable quantities in Altenberg near Aix-la-Chapelle, in Sardinia (Iglesias), Spain, and the United States of North America (New Jersey, Pennsylvania, Missouri and Wisconsin).

WILLEMITE, TROOSTITE OR HEBETINE (Zn_2SiO_4)

This ore is an anhydrous silicate, and occurs with calamine in important quantities at Altenberg and in New Jersey. It contains 58 per cent. of zinc.

HYDROZINCITE OR ZINC BLOOM ($ZnCO_3 + 2ZnH_2O_2$)

This ore occurs in small quantity in many deposits of zinc ore; it is abundant near Santander. It contains 57·1 per cent. of zinc.

ZINCITE OR RED ZINC ORE (ZnO)

This ore is coloured red by oxide of iron, and always contains oxide of manganese, the proportion of manganese going up to 12 per cent. It occurs abundantly in the State of New Jersey. When pure it contains 80·2 per cent. of zinc.

FRANKLINITE ($3(FeZn)O + (FeMn)_2O_3$)

This ore occurs with zincite in New Jersey; it contains 11 to 21 per cent. of zinc.

METALLURGICAL PRODUCTS CONTAINING ZINC

Besides its ores, certain furnace products form sources of zinc extraction. Among these are the so-called *furnace calamine* (furnace deposits obtained during the smelting of lead, copper, silver and iron ores containing zinc, and which are largely composed of zinc oxide), zinciferous flue dust, zinc fume, zinc dross, roasted silver ores containing zinc. Zinc is obtained as a bye-product in the treatment of alloys of zinc and silver, zinc, silver and lead, and zinc, silver, copper and lead.

THE EXTRACTION OF ZINC

Zinc may be extracted from ores and furnace products by means of:—

1. The Dry way.
2. The Wet way, up to a certain point (combined wet and dry way).
3. Electro-metallurgical methods.

Metallic zinc can only be obtained in the dry way and electro-metallurgically. As zinc cannot be separated from its solutions by means of any of the metals that resist ordinary temperatures, the wet method only admits of the production of compounds of zinc (zinc oxide), from which the metal must be extracted in the dry way. Wet methods can therefore only be considered as accessory processes in the dry method of zinc extraction.

The extraction of zinc from ores and furnace products in the dry way is performed by converting the zinc into an oxide (unless it already exists as oxide or silicate in the ores, or as an alloy in furnace products), followed by the reduction of the oxide or silicate by means of carbon. Furnace products which consist of mixtures of zinc oxide and metal, are submitted to direct reduction. From alloys with metals less volatile than zinc, the latter is obtained by simple distillation. The direct extraction of zinc from its sulphide by heating the latter with carbon and lime has not proved successful.

The extraction of zinc by the combined wet and dry methods is performed by dissolving out the zinc, converting the zinc in solution into an oxide, and then reducing the latter by means of carbon. The electrolytic extraction of zinc is performed by obtaining the zinc in the form of aqueous solutions, from which zinc is separated by means of the electric current. If zinc exists in the form of alloys the latter may be used as anodes in the electric circuit. Of all the above methods, the dry way should be given the preference whenever the ores or furnace products are sufficiently rich in zinc. In spite of the great deficiencies, to be considered below, of the latter process, no success has attended attempts to replace it advantageously by combined wet and dry, or electro-metallurgical methods. The combined wet and dry method has been tried experimentally on poor ores, but has hitherto failed, on account of a number of defects and of the high expense attached to it. It has only been employed definitely in cases in which the object was not the extraction of metallic zinc, but the separation of zinc from other metals or metallic compounds, so that the zinc is obtained as a bye-product in the form of commercial compounds, such as sulphate, chloride, basic carbonate or oxide of zinc. It is not, however, quite impossible but that it may find employment in zinc extraction proper as an auxiliary to the dry method for the preparation of compounds rich in zinc from ores or products poor in that metal. The electro-metallurgical method has, up to the present, only been used on an experimental scale, and with varying results upon zinc ores proper, containing no other valuable metal except zinc. Although the technical possibility of this process has been proved for such ores by continuous operation for a certain time, it is still to-day an open question whether it is superior to the dry method. It can be used with advantage for alloys which form anodes soluble in the electric circuit. It has also been used recently for the extraction of the zinc from pyritic residues, and is to be used shortly for the extraction of zinc from intimate mixtures of argentiferous zinc and lead ores which cannot be completely separated by dressing (at Broken Hill, N.S.W.).

Purification of Zinc

The zinc that has been obtained by the dry or combined wet and dry methods, is in most cases contaminated by impurities, such as lead and iron, which interfere with the technical applications of the former metal. It, therefore, needs a previous purification, known as refining. This refining is executed in the dry way.

EXTRACTION OF ZINC IN THE DRY WAY

The Extraction of Zinc from Ores

The method of extracting zinc in the dry way, which has been used up to the present for ores, depends upon the property of carbon and bodies containing carbon to separate metallic zinc from the oxides and silicates of that metal at a high temperature. The recent suggestions to decompose sulphide of zinc by means of iron [1] have not yet been put into execution.

The ores from which zinc is extracted are the oxide, silicate, carbonate and sulphide. The ores consisting of oxide and silicate contain zinc in a combination suitable for reduction. Ores containing the carbonate can be converted into oxide by simple calcination; those that contain the sulphide by means of an oxidising roasting. The complete reduction of oxide of zinc only takes place at very high temperatures. It begins even below the boiling point of zinc at a moderate red heat, but is only complete at a bright redness approaching a white heat. It is therefore necessary to increase the temperature to the boiling point of zinc, so that the zinc is separated in the gaseous condition, and requires to be condensed to fluid zinc.

The chemical reactions in extracting zinc from its oxide and silicate consist in the formation of zinc and carbon monoxide, when the former compounds are heated to the necessary temperature with carbon. Carbon monoxide, however, also has a reducing action upon the oxide of zinc, carbon dioxide being produced. Carbon dioxide, which oxidises zinc at a red heat, is again reduced immediately upon its formation to carbon monoxide by means of the carbon, which must be present in excess, the carbon monoxide thus formed again reducing a further amount of zinc oxide. Oxidation of the zinc by carbon dioxide is therefore impossible in the presence of a sufficient excess of carbon. It is unknown to what extent carbon monoxide assists in the reduction of zinc oxide. The more intimate the mixture of zinc oxide with carbon, the better does the reduction of the former take place.

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[1] English Patent, No. 5,029, 1887; German R. Patent, Biewend, No. 81,868, August 7, 1894.

The gaseous zinc must be condensed to the fluid state; as zinc vapours are oxidised by air, water vapour and carbon dioxide, they must not be allowed to come into contact with these gases. The condensation of zinc vapour to fluid zinc, which forms the most difficult portion of the process of zinc extraction, only takes place between definite limits of temperature, and is then only possible when the zinc vapour is not too greatly diluted by other gases. If the temperature falls below the melting-point of zinc (415° C.), the zinc vapours condense to a powder known as *zinc fume*. If the temperature greatly exceeds 550° C., the zinc remains in the gaseous form. If the zinc vapours are mixed with foreign gases, their condensation to fluid zinc is thereby rendered more difficult. When a certain point of dilution with foreign gases is reached, the zinc vapours will no longer condense to fluid zinc, but form zinc fume on cooling down. The temperature, at which zinc vapours, produced in practice by the reduction of zinc oxide by carbon, and therefore diluted with carbon monoxide, will condense to fluid zinc, lies between 415° and 550° C. The necessity of employing a temperature exceeding the boiling-point of zinc in the extraction of that metal, the readiness with which zinc vapours are oxidised by air, carbon dioxide and water vapour, and especially the difficulty of condensing into a fluid form the vapours of zinc diluted by other gases, cause the extraction of zinc to be one of the most difficult and most imperfect of all metallurgical operations. The readiness with which zinc vapour is oxidised compels the process of reduction to be carried on with the exclusion of air. The high temperature required for the reduction renders necessary the employment of a first-class fire-resisting material for the construction of the apparatus of reduction. The latter are at present closed vessels, such as tubes or muffles, made of fireclay, with a comparatively small capacity, and destroyed with comparative ease, so that the operation is attended with high costs in fuel and labour. As it is not possible to completely condense zinc vapours, as the walls of the apparatus of reduction are, to a certain extent permeable by gases, and readily fractured, as the material of the retorts always retains a certain quantity of zinc in the form of an aluminate, and as a certain quantity of metal always remains in the residues, the extraction of zinc is accompanied with considerable losses of metal—amounting in favourable cases to about 10 per cent. of the zinc contents of the ore, and in some cases rising to 25 to 30 per cent. For the above reasons, ores, the percentage of zinc in which falls below certain limits, can no longer be treated with profit in the dry way.

It is therefore intelligible that attempts should have been made for a long time to improve this defective process of zinc extraction. The process of distillation can only be avoided by means of electrolysis, because zinc is not precipitated in the metallic state from its solutions by any metal capable of existing at the ordinary temperatures, on account of its highly electro-positive character. Up to the present, however, the electrolytic extraction of zinc from its ores has not shown any superiority to the process of distillation as now carried on.

The numberless attempts to conduct the extraction of zinc oxide in reverberatory and blast furnaces have only given negative results as far as regards the production of zinc in the metallic state. By the employment of reverberatory furnaces zinc oxide only can be produced; by the employment of blast furnaces zinc vapour can certainly be produced; the latter has, however, even when heated air was employed, been found to be so greatly diluted by carbon monoxide and nitrogen, that it was impossible to condense it to the fluid state: only zinc fume can be separated from it. It appears, therefore, that blast furnaces can only be used for the production from ores, of intermediate products rich in zinc, such as mixtures of zinc fume or zinc powder with small quantities of zinc oxide, from which latter the zinc can only be obtained by treatment in retorts. Hence it happens that improvements in the extraction of zinc in the ordinary way, apart from the calcination of zinc-blende, have been confined to the distillation process in closed vessels. Many such improvements may be mentioned, *e.g.*: the introduction of gas-firing, the improvement of the fireproof material of the vessels employed, the production of dense vessels by means of pressure, the increased size of the furnaces, the more perfect appliances for the condensation of zinc vapour and for the removal of the products of combustion from the interior of the zinc works.

In zinc extraction, as now practised, we have to distinguish:—

1. The preparation of ores for the process of reduction by calcining or roasting.

2. The reduction process proper, or the extraction of the zinc from the calcined ores.

1. Preparation of Ores for the Process of Reduction

Zinc ores, which contain the zinc in the form of oxide, require no preparation. Silicates of zinc but rarely form an independent object of zinc extraction, as they generally occur together with calamine, and are therefore treated in the same way as that ore. If they occur by themselves, they have to be calcined for the removal of the water, which would otherwise exert an oxidising action upon the zinc during the process of reduction. No other preparation is required, because zinc is reduced from its silicates by means of carbon. Silicates free from water require calcination only to make them tender; ores of zinc that contain the metal as carbonate and sulphide—viz., calamine (including zinc bloom) and blende—must be converted into oxide before they can be reduced.

Zinc could be reduced from calamine without converting that ore previously into oxide; but in this case the process would not only be seriously delayed by the expulsion of the carbon dioxide and water from the ore and the loss of heat thereby occasioned, but the products, carbon dioxide and water vapour, would exert an oxidising influence upon the zinc vapour produced. To avoid these objections, it is absolutely necessary to drive off the water and the carbon dioxide from the calamine by a decomposing roasting known as burning or calcining. This operation also possesses the great advantage of making the calamine more porous in structure. The reduction of zinc is hereby greatly facilitated, as an opportunity is afforded for the carbon monoxide to penetrate through all portions of the calamine thus rendered spongy, and to exert its reducing influence upon it.

Zinc blende must be converted into zinc oxide by means of an oxidising roasting combined with a decomposing roasting that shall decompose the zinc sulphate formed.

Crushing Zinc Ores

Of the above ores, zinc blende requires for its perfect calcination to be broken down to 0·04 to 0·08 inch mesh. Such crushing is also necessary in the case of pieces of blende which have been previously roasted in heaps, stalls or shaft furnaces before the final roasting. Whenever the blende is not produced in the form of concentrates by dressing works, the ores are crushed in rolls or edge mills after being previously broken with rock breakers in case of need. In Upper Silesia, Schwarzmann's friction rolls have been found to be exceedingly effective and durable. As calamine can be burnt in lumps, it only needs crushing after burning. The Belgian method of zinc reduction requires more complete crushing than does the Silesian method. For hard ores, such as silicate of zinc and willemite, rolls, for soft ores, edge runners, ball mills and disintegrators are employed. When the ore has thus been obtained in the necessary form, it has to undergo a preliminary treatment, either by :—

(*a*) Burning or calcination of calamine.
(*b*) Calcination of zinc blende.

(*a*) *Burning or Calcining of Calamine*

The object of this process is to remove carbon dioxide and water from the ore and to make it more porous. If other bodies containing water and carbon dioxide are mixed with the calamine, the water or carbon dioxide must be driven off from them also. This object is attained by heating the calamine to such a temperature that the carbonate of zinc shall be decomposed into zinc oxide and carbon dioxide, which temperature must also be sufficient to decompose any foreign carbonates present. Calamine gives up its carbon dioxide at a moderate red heat, whilst the complete decomposition of calcium carbonate requires bright redness. The loss of weight of pure zinc carbonate on complete calcination amounts to 35·5 per cent.; when all the water is removed from silicate of zinc, this loses 7·5 per cent. As a general rule, burnt calamine still retains more or less carbon dioxide, up to some 17 per cent.

As the zinc oxide produced by burning calamine gradually attracts carbon dioxide from the air, whilst lime does so rapidly, it is necessary to treat burnt calamine soon after it has been calcined, but immediately, if it contains much lime. Calamine may be burned in heaps, stalls, shaft or reverberatory furnaces. As a rule, burning in heaps and stalls, for which lump ore is necessary, is to be avoided on account of the imperfect decomposition of the ore and the great waste of fuel. It is far more costly than the roasting of sulphides in heaps and stalls, as in the latter case the greater portion of the heat required for the operation is produced by the combustion of sulphur, whereas the heat required to remove water and carbon dioxide from calamine can only be produced by the combustion of extraneous fuel. Burning in heaps, with wood for fuel, is practised, according to Thum,[1] in the north of Spain; burning in stalls, according to the same authority, in the mountains of the south of Spain, where wood is scarce. As a rule, lump calamine should be burnt in ordinary shaft furnaces or in shaft furnaces fixed by means of external grates, crushed ores in reverberatory furnaces. The grate-fired shaft furnace has this advantage over the ordinary shaft furnace, that the ashes of the fuel do not intermix with the burnt ore, as is the case when fuel and ore come into direct contact inside the ordinary shaft furnace.

Burning Calamine in Shaft Furnaces

Calamine can be burnt in ordinary shaft furnaces with a comparatively small consumption of fuel, about 3·6 per cent. of the weight of the ore. This method admits of a high production, and requires but little labour; it has, however, the objection that the burnt ore is mixed with the ashes of the fuel. If, moreover, the temperature rises too high, some zinc may be reduced. The fuels employed are lean coals, low in ash, lignite low in ash, small coke low in ash, or small charcoal. These are charged in layers alternating with layers of calamine into the furnace. Together with the lump ore, the charge may contain a certain amount—15 or 20 per cent.—of ore fines.

The furnaces do not differ in any important respect from lime-kilns. The older furnaces have boshes and heavy retaining walls. The latter can be replaced with advantage by a casing of iron plates. The height varies, according to the nature of the ore, from 10 to 20 feet, and the diameter from 3 to 10 feet. The bottom is either flat, or provided with a cone. The output varies according to the nature of the calamine and its impurities, and the size of the furnaces. It is lower the greater the proportion is of lime and zinc-blende. Under favourable circumstances, with large furnaces it may amount to 25 or 30 tons per 24 hours. The fuel consumption also varies with the impurities of the ore, and may lie between 3 and 6 per cent. of the weight of the raw ores. Calamine is burnt in shaft furnaces in Moresnet (Belgium), Dortmund, Laurion, Lehigh (Pennsylvania), and in the district of Iglesias (Sardinia). At Altenberg, near Moresnet, a mixture of calamine and silicate of zinc used to be burnt in a shaft furnace of the construction shown in Fig. 1,[2] in which *k* is the lining, *r* the retaining wall, *v* the cone, *g* arches, of which there are four, giving access to the draw-holes *z*. The shaft is 7 feet 3 inches in diameter at the throat, 9 feet 8 inches in the centre, and 5 feet 6 inches at the draw-holes. The cone is 3 feet 6 inches high; the height of the furnace from the point of the cone to the throat is 17 feet 6 inches. In this furnace calamine mixed with some silicate of zinc was burned with lean coals and coke smalls. The layers of ore, which alternated with layers of fuel, were 6 inches deep; 25 tons of ore were burned in 24 hours, during which time there were six drawings. The consumption of fuel was from 3 to 4 per cent. of the weight of the ore, and the loss of weight was about 27 per cent. of the weight of the raw ore. Any silicate of zinc, or any ferriferous calamine, were removed from the burnt ore by hand dressing, and after crushing were burned again. At Montefiore, near Iglesias, where shaft furnaces are used which have a conical grate instead of a simple cone, small charcoal is used as fuel, from 4 to 6 per cent. of the weight of the ore being consumed.[1]

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[1] *Bemerkungen uber Zink-Industrie, B. u. H. Ztg.*, No. 17, p. 138, 1876.

[2] Thum, *Zinkhuttenbetrieb der Altenberger Gesellschaft. B. u. H. Ztg.*, p. 405, 1859, and p. 4, 1860; Kerl, *Metallhuttenkunde*, p. 433, 1881.

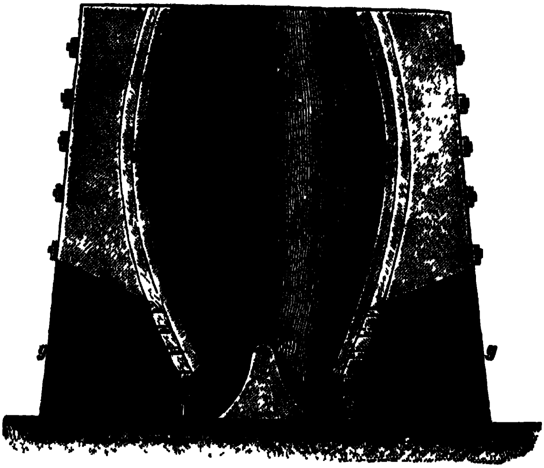

Fig. 1.

Burning Calamine in Grate-fired Shaft Furnaces

Burning lump calamine in grate-fired shaft furnaces yields a product which is not contaminated by the ashes of the fuel, though it may at times contain small quantities of flue-dust. There is also less danger of the reduction and volatilisation of zinc, than when the ore comes in direct contact with the fuel; but, on the other hand, the fuel consumption is greater than in the simple shaft furnace. Only raw fuel or gas can be used for heating purposes. The consumption of raw fuel amounts, according to its nature and that of the ores, to some 6 to 9 per cent of the latter. The furnaces are constructed like limekilns, fired by external grates; they are circular in horizontal section and contracted below. Their height is 8 to 16 feet; their diameter, in the upper widest portion of the shaft, 5 feet to 5 feet 9 inches, at the narrowest portion, at the fireplace, 1 foot 8 inches to 2 feet. The number of fireplaces, which are disposed laterally about the lower portion of the furnace, is either 1 or 2. The output varies with the size of the furnace, the nature of the ores, and the number of fireplaces, lying between 6 and 14 tons per 24 hours. Such furnaces are employed in the south of Spain.

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[1] *Oesterr. Zeitschrift*, No. 40, 1886.

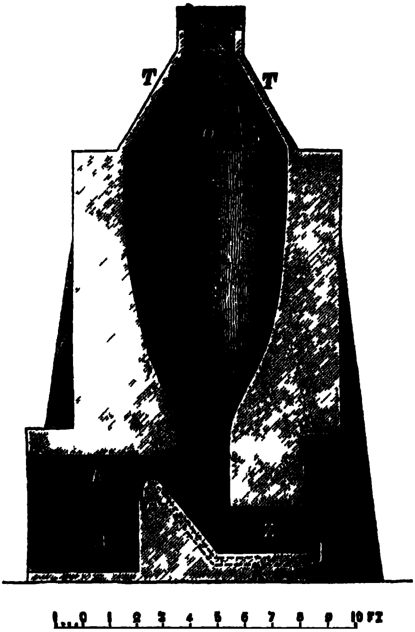

FIG 2.

The construction of such a furnace, with but one fireplace, is shown in Fig. 2.[1] *S* is the shaft, *R* the fire-grate, *Z* the opening through which the burnt ore is drawn. The ashpit *A* below the fireplace is closed, air required for combustion entering through a flue *K* in the brickwork of the furnace, in which it is heated before it enters at the grate The calamine to be burned is charged through the opening *O*. The throat of the furnace is covered by a conical hood *J*, which terminates in a short flue *W*, and is provided in its upper part with a damper to regulate the draught. In such a furnace with one fireplace, 5 to 8 tons of burnt calamine are produced in 24 hours, with a coal consumption of 8 to 9 per cent. of the weight of the burnt ore. The raw ore loses at least 10 per cent. of its weight by burning. In a furnace of equal size, with two fireplaces, about 10 tons of burnt ore were obtained in 24 hours with the same fuel consumption. Six men are required per 24 hours to work the furnace.

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[1] *Berg und Hutten Ztg.*, p. 360, 1862.

Burning of Calamine in Reverberatory Furnaces

In such furnaces ore fines alone can be burnt satisfactorily; lumps are far better burnt in either of the above shaft furnaces. Reverberatory furnaces require more fuel and labour than do shaft furnaces, but, if well constructed, yield as great an output as do grate-fired shaft furnaces, viz., 8 to 10 tons in 24 hours. Reverberatory furnaces are employed of various forms, viz., with fixed hearths, with movable hearths, furnaces independent of zinc reduction furnaces, and reverberatory furnaces which are heated by the waste heat of the zinc reduction furnaces. Those reverberatory furnaces which are worked independently are either gas-fired or fired by a grate. Wherever calamine is burnt at the mine, which is the better way whenever fuel is cheap there, and the ore has to be transported considerable distances to the smelting works, it is of course necessary to work the reverberatory furnaces independently. Wherever calamine is burnt at the smelting works, it is preferable to conduct the burning quite independently of the work of the reduction furnace, and to use the waste heat of the latter for warming the air used for combustion, or in the case of gas firing for heating up the gas. Only in such cases in which the furnace gases, after having thus been utilised, still retain sufficient heat to be able to expel water and carbon dioxide from the calamine, is it profitable to use them for burning this ore.

Independent Reverberatory Furnaces

Fixed Reverberatory Furnaces

Such furnaces have to be worked as a general rule by hand-power. Only when labour is exceedingly dear is it possible to use with advantage fixed furnaces in which the ore is rabbled mechanically.

Fixed Reverberatory Furnaces Worked by Hand

As a rule, the best furnace of this type for burning calamine is the long-bedded continuous-acting furnace, the so-called *Fortschaufelungsofen*. In these the ore is charged at the coldest part of the furnace by the flue-bridge, and is shovelled gradually from this point to the hottest part of the furnace at definite intervals of time, until it is ultimately drawn out at the fire-bridge in the burnt state. Furnaces worked intermittently, in which the whole of the charge of ore which is to be burnt, is charged in at one time, and is drawn out at one time, when the operation is complete, are not to be recommended on account of their high cost for labour and fuel. Long-bedded calciners with only one hearth are to be preferred to furnaces of this type with two hearths lying one above the other, because working on the upper hearth is inconvenient, and when one of the hearths needs repairing the whole furnace must be let out. Furnaces with two or even three hearths, one above the other, should therefore only be employed when ground space is either very valuable or not to be got. The hearth either lies horizontally, or has a certain inclination (Ferraris furnace). The reverberatory furnace for burning calamine differs from those used for calcining the sulphides of iron, silver, copper or lead, in that it is shorter and narrower than the latter. It must not be forgotten that when the above-named sulphides are calcined, a considerable amount of heat is developed from the ores themselves; that the air required for their calcination enters by the working doors; and that as long as it is not in excess, it becomes itself a source of heat on account of its action upon the sulphides. On the other hand, when calamine is burnt, no heat is developed from the ores, nor is any access of air necessary. In order to utilise the heat of the fuel to the best purpose, it is therefore necessary to have only as many working doors as are absolutely required for the satisfactory rabbling and turning over of the ores. It is also useless to give the hearth any excessive length or breadth, because the removal of the carbon dioxide requires a comparatively high temperature, whilst no heat is developed from the ore, as occurs in the case of sulphides even close to the flue-bridge.

The length of the hearth should not exceed 40 to 43 feet. With a double hearth and a single fireplace, the length of the two hearths together should not exceed the above amount. When gas-firing is used, the length of the hearth may be somewhat longer, up to 46 feet for instance. The grate-fired furnace with double hearth at the works of the Altenberg Company is 40 feet, including the upper and lower hearths. Another direct-fired furnace at Letmathe, near Iserlohn, in Westphalia, in which calamine was formerly burnt, possessed two hearths lying one above the other, with a total length of 27 feet. The gas-fired furnaces of Ferraris, with inclined hearth, at Monteponi, near Iglesias, has a total length of 43 feet 6 inches.

The breadth of the hearth should not exceed 8 feet, because otherwise the ore upon the hearth cannot be satisfactorily rabbled and turned over with working doors along one side only. For instance, the Letmathe hearth was 6 feet 2 inches wide, the hearth of the Altenberg Company's furnace was 7 feet 6 inches wide, whilst the gas furnace at Monteponi has a hearth 8 feet 2 inches wide. The height of the arch of the working chamber should be about 1 foot 4 inches to 2 feet at the outside. In order to utilise the heat to the utmost, it is advisable to incline the arch somewhat towards the flue-bridge, or else the hearth may have a gradual slope upwards, or may rise by steps towards the flue. The hearth may be made of ordinary brick, fire-brick being only required in the neighbourhood of the fire-bridge. The working doors are placed from 6 feet to 8 feet 2 inches apart, centre to centre. The quantity of calamine that can be burnt in 24 hours depends upon the nature of the impurities, the size of the furnace and the character of the fuel. It varies from 3 to 10 tons per furnace, the fuel consumption being between 10 and 15 per cent. of the weight of the raw ore. Each furnace requires two to three attendants per shift. The construction of a reverberatory furnace fired by grate, as built at the works of the Vieille Montagne Company, is shown in Figs. 3 and 4. The furnace has two hearths, *H* and *J*. The calamine is first dried on the arch *G* above the upper hearth, and is then let down on to that hearth by means of openings *o*, which can be closed when desired. After remaining 6 hours on that hearth, it is removed to the lower hearth through openings *p*, and after 6 hours further is emptied into the vaults *K* through the openings *q*. *F* is the firegrate, *T* the flue through which the products of combustion pass into the stack, *a* are the working doors, which can be closed by sheet iron. Fig. 4 shows a plan of the upper hearth with the openings *p*. The openings *q* for emptying the calamine into the cooling vaults lie at the opposite side of the lower hearth. In 24 hours 4 charges, weighing together 8 tons, are calcined in this furnace, with a consumption of 2·90 to 3·11 cubic feet of coal.[1]

At the works near Cilli, in Austria,[2] finely ground calamine is calcined in long-bedded furnaces, which are built in pairs with their long sides adjoining, and with 4 working doors at the opposite sides. They are fired with lignite by means of special grates. In 24 hours 7 charges of 12 cwts. each are worked off. One cwt. of coal is required for 3 tons 4 cwts. of calcined ore.

At the Paul Works, near Rosdzin, in Upper Silesia, there are three long-bedded calcining hearths, one above the other, each of which has its own fireplace. Each hearth is 17 feet 10 inches long and 7 feet 10 inches wide On each hearth 15 tons of calamine are calcined in 24 hours, with a consumption of 1·5 tons of coal The furnace is worked by one man, taking a 12-hour shift. The arrangement of a reverberatory furnace fired by gas (the Ferraris furnace), as used at the Monteponi mines, is shown in Figs. 5 and 6.[1]

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[1] Thum, *loc. cit.*

[2] *Berg. und Hütten. Ztg.*, p. 31, 1894.

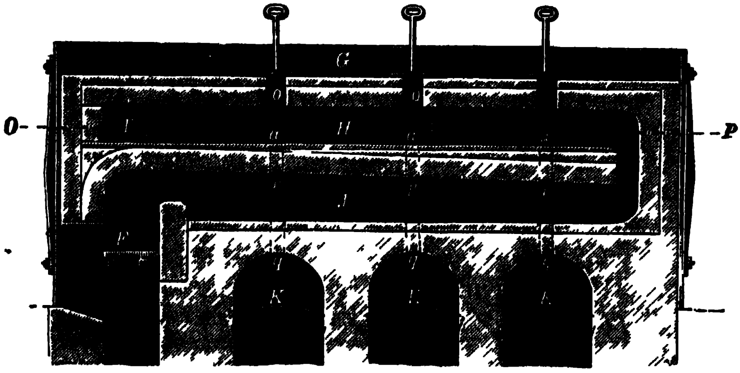

Fig 3

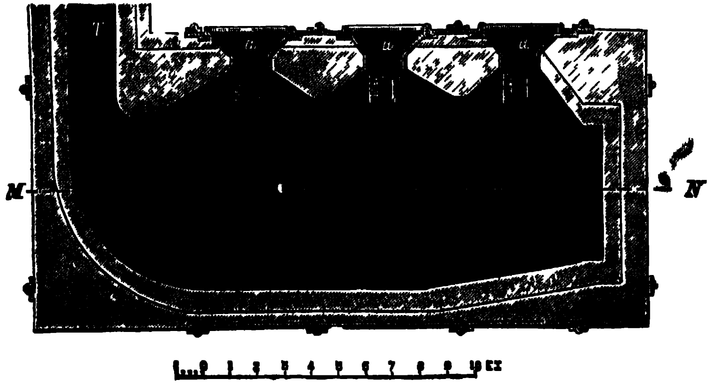

Fig 4

Two furnaces A and B, with inclined hearths are built side by side with a back wall in common. There is a gas producer G on the Boetius system, common to both furnaces The ores are charged at the upper end of each furnace through a hopper Z and pass through the upper to the lower end. The double furnace treats 20 tons of ore in

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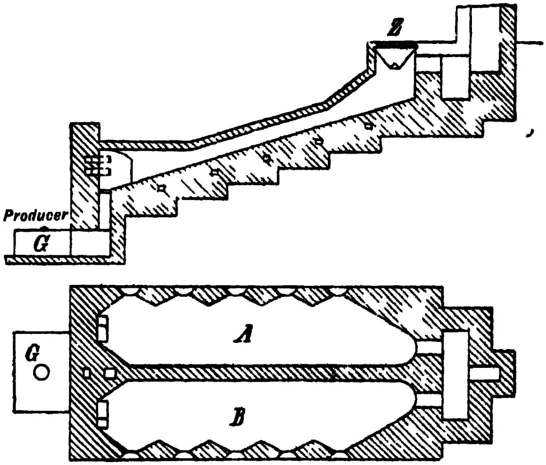
[1] Marx. *Zeitschrift fur Berg Hutt - u Salinen wesen*, vol xl

24 hours, with a consumption of Cardiff coals equal to 15·11 per cent. of the weight of the raw ore. Five men are employed to work the two furnaces. The ore loses 23 per cent. by calcination.



Figs 5 and 6.

Fixed Reverberatory Furnaces worked Mechanically.

Such furnaces appear to be nowhere in use for calamine, unless the ore contains a considerable quantity of zinc-blende mixed with it. Their use would only be indicated in the case of abnormally high wages. Under such circumstances the furnaces of O'Harra, Vol. I., p. 72, the Pearce furnace, Vol. I., p. 75, and the Horseshoe furnace of Brown, Vol. I., p. 76, would probably be the most suitable, because their output is far greater than that of fixed reverberatory furnaces worked by hand, or of Parkes's mechanical furnace, Vol. I., p. 78.

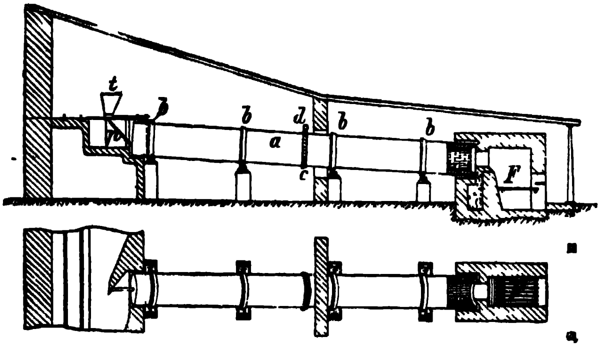
Reverberatory Furnaces with Movable Hearths

Calciners of this type, with fixed or movable rabbles, can scarcely be applied with advantage to the burning of calamine, on account of their comparatively small output. Many such furnaces may be mentioned, *e.g.*, that of Brunton, which is used for the roasting of tin ores containing arsenical pyrites, and the furnace of Gibbs and Gelstharpe, Vol. I., p. 230, which is used for the chloridising roasting of cupriferous pyrites residues.

Reverberatory Furnaces with Movable Chambers

Such furnaces may be used when wages are high. They consist of rotating cylinders, which work either intermittently or continuously. Furnaces worked intermittently, which are used with advantage for the calcination of copper ores, and of which the best known is the Bruckner furnace, Vol. I., p. 80, have not been employed for the burning of calamine, as far as the author knows. Of the furnaces worked continuously, that of Oxland is used with advantage in the mining district of Iglesias. Figs. 7 and 8 show the construction of such a furnace as used at the Monteponi mine.[1]

In these figures *a* is the inclined rotating cylinder lined with fire-brick, *b*, *b* are friction rings resting on rollers, *c* is a toothed wheel worked by the tangent screw *d*, the latter being driven by a steam engine. The ore is charged through a hopper and falls from it on to a cast-iron plate, which forms the cover of the furnace, and upon which it is dried. Thence it passes through the hopper *t* into the tube *p*, through which it slips down into the cylinder. In consequence of the slow revolution of the cylinder, which turns 15 times in the hour, the ore gradually reaches the lower end, when it drops out in the calcined condition. *F* is the firegrate. The mixing of the ore is promoted by 4 ploughs arranged inside the cylinder; 12 tons of ore are calcined in 24 hours, the consumption of Cardiff coal amounting to 12 41 per cent. of the weight of the raw ore. The loss of weight amounts to 28 per cent. Two men on a shift work these furnaces.



Figs 7 and 8

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[1] Marx, *loc. cit.*

Reverberatory Furnaces, heated by the Waste Heat of Zinc-Reduction Furnaces

Such reverberatory furnaces may be combined with Silesian or with Belgian zinc-reduction furnaces. With the former they are placed between two or four such furnaces, or in front of them, whilst in the latter case they are built above them. The reverberatory furnaces are composed of flat brick arches over hearths of varying shape and size. A calcining furnace combined with a Belgian zinc-reduction furnace, such as was formerly in use at Moresnet, is shown in Figs. 9 and 10. The products of combustion from the reduction furnaces enter the furnace body *h* through the slot *k*, and escape from the former through the flue *f* into a stack 23 feet in height. The ores are charged with the furnace through an opening *z* in the crown of the arch. The burnt ores are discharged through a vertical flue *w* into a vault *g* built below the furnace. At *p* there are working doors through which the ores in the furnace can be rabbled. A furnace of this kind will calcine from 36 cwt. to 2 tons of calamine in 24 hours.

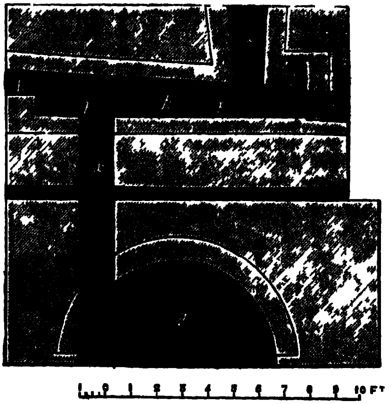

Fig. 9

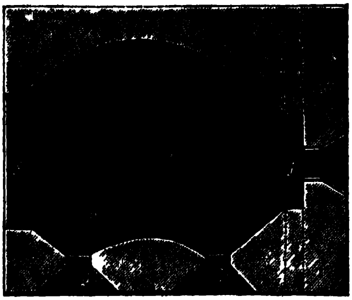

Fig. 10

Calcining furnaces attached to Silesian smelting furnaces have areas of from 10 to 53 square feet, and are connected with both the older and some of the newer forms of these furnaces. They have, however, an injurious effect upon the output of zinc both by reason of cooling the furnace walls, as also by interfering with the draught, and have, therefore, been entirely discarded in the most recent furnaces, or have been erected at some distance from them. The calcining furnaces attached to the various types of Silesian furnaces will be found fully shown in the illustrations of the latter. Both crushed calamine and lump ore can be burnt in these furnaces.

The calciners of the older Silesian furnaces have an area of 53 square feet. In these 1·5 tons of calamine are burned in 12 hours. In the calciners of the stack-furnaces, which have an area of 10 square feet, 8½ cwts. of calamine can be roasted in 8 hours. In the calciners of the blast-fired furnaces, which have an area of 16·8 square feet, 14 cwts. can be burned in 8 hours.

At Lipine, where reduction furnaces, fired with gas, and heating shafts are used, a small calciner is placed on either side in the middle of the furnace block. Its length is 7 feet 3 inches, its breadth 2 feet 8 inches, and its height 2 feet 4 inches. In 24 hours, from 2 tons 5 cwt. to 3 tons of calamine can be calcined. The labour is provided by the men in charge of the reduction furnace. On the average, burnt Upper Silesian calamine retains some 17 per cent. of carbon dioxide.[1] Such of the latter as does not escape before the reduction of the zinc oxide, must be reduced to carbon monoxide by an excess of carbon in the muffles.

(*b*) *Calcination of Zinc Blende*

The object of calcining zinc blende is to convert the sulphide of zinc into oxide by means of atmospheric air. Simultaneously the other sulphides contained in, or mixed with, the zinc blende are also converted into oxides. Any carbonates intermixed with the blende have also to be converted into oxides. From any arsenical and antimonial compounds that may be present, the arsenic and antimony must, moreover, be volatilised as completely as possible. The calcination must be conducted so that as little sulphur as possible remains in the calcined ore, because sulphide of zinc, whether it be present in the form of zinc blende that has remained undecomposed, or whether it is produced during the reduction process by the reduction of zinc sulphate, remains undecomposed when the zinc is reduced, so that its zinc contents are lost for the extraction of zinc. The complete removal of sulphur from the ore is, however, only exceptionally attained, because in calcination the last portion of sulphur can only be driven out with great difficulty, and because the formation of zinc sulphate, which is only completely decomposed at a red heat approaching whiteness, is unavoidable. Moreover, blende is often accompanied by substances such as galena, chalcopyrite, stibnite, and silicates of iron and manganese, which are inclined to sinter or melt at high temperatures. These envelope particles of blende and prevent the oxygen of the air from acting upon them. Under these circumstances, it is quite unavoidable that small portions of sulphur, say 1 to 2 per cent., should remain in the calcined ore. To obtain as complete a calcination as possible, it is necessary that the blende should be crushed down to a mesh of 0·04 inch, or, at the outside, of 0·08 inch, and for the decomposition of the basic sulphate formed the final temperature must be proportionately high. A high temperature entails, on the other hand, the objections that zinc oxide is volatilised, that it is reduced to zinc when brought in contact with the particles of carbon in the flame, and that the ore may be sintered or fused. Zinc sulphate can only be imperfectly decomposed by mixing carbon with the calcined ore. When pulverulent zinc blende containing only sulphide of zinc is calcined, as soon as the temperature rises to a low redness the sulphur is oxidised to sulphur dioxide, and the zinc which was combined with this sulphur is converted into oxide. The sulphur dioxide is in part volatilised, in part it is converted by contact with the red-hot portions of the ore and of the furnace walls into sulphur trioxide, which latter combines with a portion of the zinc oxide to form sulphate. The lower the temperature, and the more the zinc blende is intermixed with other sulphides, the more zinc sulphate is formed. Thus in some experiments by the author, when an intimate mixture of equal parts of zinc blende and galena from the Broken Hill Mines in New South Wales was calcined at low redness, 40 per cent. of the zinc contents of the blende was converted into zinc sulphate. The formation of zinc sulphate is promoted more by the presence of pyrites than by that of any other sulphides. When the temperature is raised to a cherry-red, the neutral zinc sulphate is split up into basic zinc sulphate and to sulphur trioxide or sulphur dioxide and oxygen. By further raising the temperature to the fullest red heat, the basic zinc sulphate itself is decomposed in the same way. Schlapp found that during the decomposition of zinc vitriol dehydrated as completely as possible, by means of heat on a large scale, some 30 per cent. of the sulphur trioxide escaped as such, whilst the remainder was split up into sulphur dioxide and oxygen.

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[1] *Steger*, *Eisen u. Metall.*, p. 67, 1888.

If the calcination takes place in reverberatory furnaces, any carbon monoxide present in the products of combustion has a reduring action upon the zinc oxide at the high temperature required to split up the basic zinc sulphate. The zinc vapours thus formed are sarried off, and are at once oxidised again by the air and the carbon dioxide present, so that loss of zinc is thus incurred. With a sufficiently long continued calcination and the employment of a sufficiently high temperature, it is, as above shown, possible to convert the whole of the zinc sulphide into oxide. As a rule, however, in consequence of the difficulty of completely decomposing the basic sulphate and of oxidising the last portions of the sulphide of zinc present, small quantities of sulphur remain in the ore. In a series of experiments[1] the following decrease in the percentage of sulphur in the ore was found on roasting three different grades of ore in a Hasenclever furnace with three muffles lying one above the other:—

PERCENTAGE OF SULPHUR IN THE ORE.

	No. 1 Ore.	No. 2 Ore.	No. 3 Ore.
Blende before charging .	19·2	26·8	26·5
On leaving the first muffle	17·6	19·1–19·9	15·9–21·4
On leaving the second muffle	12·0	11·2–14·3	9·9–12·4
On leaving the third muffle .	3·4	1·02–1·48	0·75–1·06
On drawing from the furnace .	0·6	0·35–1·02	

The temperature in the first or uppermost muffle was from 580° to 690°, that of the two lower ones 750° to 900° C. If the blende contains, as is often the case, sulphide of iron isomorphously intermixed, magnetic oxide and iron sulphate are at first produced. As the temperature increases, the magnetic oxide is converted into ferric oxide, whilst the sulphate of iron is converted into sulphur dioxide and oxygen and basic sulphate of iron, the latter of which, when the temperature rises still further, is ultimately split up into ferric oxide and sulphur trioxide, or in part into sulphur dioxide and oxygen. This decomposition takes place far below the temperature of decomposition of zinc sulphate, and the gases produced by the splitting up of the sulphate of iron promote the conversion of sulphide of zinc into sulphate. At the conclusion of the operation, all the sulphide of iron will have been converted into ferric oxide, so that the product will consist of a mixture of ferric oxide and zinc oxide, together with small quantities of zinc sulphate and undecomposed sulphide. According to Jensch,[2] the sulphur contained in dead roasted zinc blende in the form of sulphide is said to be exclusively combined with iron. A calcination down to 0·5 per cent. of sulphur, present in the form of sulphide, would thus appear to be possible only in the case of blende free from or very poor in iron. In spite however of careful dressing operations, blende is frequently intermixed with pyrites, chalcopyrite, galena, stibnite, arsenides and sulph-arsenides, spathic iron ore, barytes, quartz, calcspar, dolomite and various silicates. It also often contains silver in extractable quantity.

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[1] *Fischer's Jahresber.*, 1890, p. 444.

[2] *Zeitschr. f. Angewandte Chemie*, 1894, p. 50.

Pyrites is converted into ferric oxide by calcination. In consequence of its ready oxidisability, it promotes the commencement of calcination and the raising of the ore to a red-heat, but at the same time causes the formation of considerable quantities of sulphate of zinc. If sulphide of iron remains undecomposed after the calcination, it has an injurious effect in the process of reduction, as it perforates the walls of the vessels employed. In the presence of quartz, ferrous silicate may readily be formed in consequence of the action of reducing gases or of soot upon the ferric oxide at the high temperature of calcination. This not only envelopes particles of blende, but also acts injuriously upon the walls of the vessels employed in distillation owing to the formation of readily fusible double silicates.

Chalcopyrite is converted on calcination into a mixture of cupric and ferric oxides, and has the same disadvantages as iron pyrites. The cupric sulphate formed by its calcination decomposes at a far lower temperature than basic zinc sulphate. As this ore is highly inclined to sinter on account of its containing sulphide of copper, it is very apt to envelope particles of unroasted zinc blende if the temperature is at all high at the outset

Galena is converted into a mixture of oxide and sulphate of lead; as galena sinters very rapidly, it is also apt to envelope particles of zinc blende, unless the temperature is kept very low at the outset. It also promotes the formation of zinc sulphate by the action of sulphur dioxide and oxygen or of sulphur trioxide upon zinc oxide or sulphide. Any lead sulphate which is not decomposed at the temperature of calcination melts just as lead oxide does at the temperature required to decompose zinc sulphate, and both substances are apt to envelope particles of the ore. In the presence of quartz, silicate of lead forms, which is also easily fusible, and envelopes particles of ore. Lead oxide, as long as it is not present in too great a quantity (under 8 per cent.), is reduced in the process of reduction to metallic lead, as long as the gases of the vessels contain carbon monoxide. The lead thus formed partly volatilises with the zinc and partly remains in the residue. When it is present in large quantities, and if oxidising gases or air are present in the vessels employed in distillation, it is partly converted into silicate of lead. This silicate of lead gives rise to the formation of readily fusible silicates, and thus rapidly destroys the walls of the vessels. At the same time, lead may be reduced from it, and alloy with the zinc.

Stibnite sinters very rapidly, and envelopes particles of uncalcined zinc blende. Its sulphur is converted into sulphur dioxide and promotes the formation of zinc sulphate. *The antimony is converted into oxide, which partly volatilises and partly forms antimoniates. The latter are also formed in part by the action of the oxide of* antimony upon sulphates. These antimoniates remain for the most part undecomposed during calcination, and therefore appear as such in the calcined ore.

Arsenides and sulph-arsenides give off their sulphur as sulphur dioxide, and a portion of the arsenic forms arsenic acid; another portion of the arsenic forms arseniates of those metals (nickel, cobalt, iron and silver) whose arseniates resist the heat. The ultimate product of the calcination consists therefore of a mixture of metallic oxides and arseniates. During the process of reduction, the latter are reduced, yielding metallic arsenic, which passes into the zinc.

Siderite is converted on calcination into magnetic oxide, which promotes the formation of readily fusible silicates during the process of reduction, and, thereby, the destruction of the vessels employed. If quartz is simultaneously present in the ore, a readily fusible silicate of iron may form even during calcination, which would envelope portions of the ore. In consequence of the ready fusibility of silicate of manganese, such double silicates are apt to be formed if the spathic ore contains manganese.

Quartz by itself has no injurious effect on calcination, as it only combines with zinc oxide at a white heat. It may, however, give rise to readily fusible silicates when pyrites, chalcopyrite or siderite are present in the ore.

Barytes remains unchanged during calcination. In the process of reduction it becomes reduced to baric sulphide, which promotes the formation of zinc sulphide.[1]

Calcite is converted partly into lime and partly into calcium sulphate. Lime, together with ferrous oxide, forms readily fusible double silicates with the silica of the containing vessels, and these silicates are apt to destroy the walls of the latter. The calcium sulphate is reduced to sulphide during the reduction of the zinc oxide, and thus gives rise to the formation of residues rich in zinc. Thum[2] states that the sulphides of the alkaline earths appear to give up half of their sulphur to zinc in the presence of free zinc and carbon.

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[1] Thum, *Berg. und Hutten. Ztg.*, 1876, p. 154.

[2] *Loc. cit.*

Dolomite behaves like calcite.

Argentite is converted into sulphate of silver, which, in the last stage of calcination, becomes decomposed into silver, sulphur dioxide and oxygen. A portion of the silver is volatilised in the last stage of *the calcination at the high temperature then prevailing.*

If readily fusible silicates, especially those of iron and manganese, are mixed with zinc blende, these will sinter in the last stage of the calcination, and envelope particles of ore.

The loss of weight, by calcination, of zinc blende varies with its impurities and with the temperature, ranging between 12 and 20 per cent. The completeness of the removal of sulphur from the crushed and roasted zinc blende when the calcination takes place in reverberatory furnaces or muffles, may be proved by the chlorate of potash test or by hydrochloric acid. The amount of sulphur in the form of sulphates, however, can only be determined gravimetrically or by titration with barium chloride.

The chlorate of potash test, which is considered the most convenient, is executed by heating an iron spoon to redness in the furnace, and melting some 30 grains of chlorate of potash in it. Upon the molten salt a small quantity of the ore to be examined is then sprinkled. If no sparks are produced, due to the presence of burning sulphur, calcination is complete. Even the presence of only a few small sparks is considered the sign of a good calcination, because in this case the sulphur has been removed down to 1 per cent. The hydrochloric acid test consists in heating a small quantity of the ore with pure zinc and dilute hydrochloric acid in a test-tube. When sulphur is present in the ore, sulphuretted hydrogen is evolved. The quantity of the latter, and therefore that of the sulphur present in the ore, is determined by means of a strip of paper soaked in acetate of lead, which takes a colour varying from light to dark brown, according to the quantity of sulphur present. The percentage of sulphur may be estimated by this test to between a half and one-quarter per cent. The colours obtained may be compared with colours which have been produced by roasted blende of known sulphur content, provided always that the tests are executed in the same manner.

The Process of Calcination

Blende can only be calcined satisfactorily in reverberatory furnaces and muffle furnaces. Calcination in heaps, stalls and shaft furnaces is only available for rendering the ore friable, or for a preliminary roasting. Calcination in such apparatus must, accordingly, be followed by calcination in reverberatory or muffle furnaces. Reverberatory furnaces produce gases which contain sulphur dioxide intermixed and highly diluted with the products of combustion, so that the sulphur dioxide cannot be utilised; such furnaces should, therefore, be used only when the utilisation of the products of calcination for the production of sulphuric acid is impracticable, on account of the absence of a market, and when the gases emitted may either be allowed to escape in the neighbourhood of the smelting works, or when they can be rendered innocuous by processes which do not cause too great an outlay. Muffle furnaces admit of as good a calcination of zinc blende as do reverberatory furnaces, and do not require much more fuel than the latter, if proper use is made of the heat developed by the oxidation of the sulphide of zinc. As these furnaces produce gases containing so much sulphur dioxide as to be suitable for the manufacture of sulphuric acid, they should be employed, as a rule, when there is a market for sulphuric acid in the neighbourhood of the works, or when the sulphur dioxide can be utilised with advantage in some other way. Before the introduction of the newer forms of muffle furnace, muffle furnaces combined with reverberatory furnaces were also used. In the muffles of these combined furnaces, sulphur dioxide was produced for the purpose of sulphuric acid manufacture, whilst the blende was roasted dead upon the hearths of the reverberatory furnaces. Their erection may be justified when there is only a limited market for sulphuric acid, so that only a portion of the sulphur dioxide contained in the gases can be worked up with advantage. Heaps and stalls can only be employed for rendering very compact blende more friable in such districts in which it is impossible to utilise the sulphur dioxide, and in which no injury is inflicted by the latter on the neighbourhood. In such cases, the calcination should be looked upon as a preliminary to the crushing of the lump ore, which has to be calcined dead in reverberatories after it has been crushed.

Shaft furnaces may be used for preliminary roasting with certain varieties of blende which burn readily, when it is only possible to utilise the gases produced to a limited extent. After this preliminary calcination, the lump ore has to be crushed and roasted dead in reverberatory furnaces, whilst blende that has been partly roasted in the form of powder goes direct to the reverberatory. If, on the other hand, it is possible to utilise the whole of the sulphur dioxide available in the calcination of the blende, calcination in muffles is to be preferred to the combined calcination in shaft and reverberatory furnaces, as the former type of furnace also admits of the utilisation of the heat developed by the oxidation of the sulphide.

We have therefore to consider :—

Calcination in heaps and stalls.
Calcination in shaft furnaces.
Calcination in reverberatory furnaces.
Calcination in combined reverberatory and muffle furnaces.
Calcination in muffle furnaces.

Calcination in Heaps and Stalls

This process can only be employed exceptionally for calcining blende in order to render it friable in districts in which no complaints are to be feared on the score of the sulphur dioxide vapours, as was the case, for instance, at the mines of the Lehigh Company of Bethlehem in Pennsylvania[1] At these mines lump ore was calcined, resting upon a grate of iron bars supported by two outer walls and one central wall, in heaps 28 feet in length, 15 feet in width, and 8 feet 2 inches high, a wood fire being applied below the grate. The calcined blende was crushed and then roasted dead in reverberatory furnaces. The employment of stalls is unknown to the author. Neither of the above modes of calcination is probably in use at the present day.

Calcination in Shaft Furnaces

Shaft furnaces are employed for the preliminary roasting of lump ore or of slimes. In both cases the sulphur dioxide that escapes during this preliminary roasting is to be utilised for sulphuric acid manufacture. The partly roasted ores are then completely desulphurised in reverberatory furnaces without any attempt being made to utilise the sulphur dioxide that escapes in this further roasting. Lump blende may be part roasted in kilns or pyrites burners; for the preliminary roasting of pulverulent blende the Gerstenhöfer furnace has come into use.

Calcination of Lump Blende in Shaft Furnaces

Kilns or pyrites burners may be employed for roasting blende in lumps.

Kilns are moderately high shaft furnaces, in which the ore to be roasted rests either upon a grate or upon a flat or saddle-shaped floor.[1] They are distinguished from pyrites burners by their greater height, and they keep the temperature better together than the latter. They are therefore specially suitable for the calcination of blendes which are low in pyrites and in sulphur. The shaft of these kilns is rectangular or square in cross section, 3 feet 3 inches to 5 feet wide in the clear, and 5 feet to 8 feet 3 inches long in the clear. As soon as the blende has taken fire, it continues to burn by itself on account of the heat generated by the oxidation of its constituents, and this produces the temperature requisite to maintain the calcination. In favourable cases the sulphur may be removed down to 6 to 8 per cent. Upon the average, the quantity of ore put through in one shaft amounts to 1 ton per 24 hours. In the Freiburg kilns, whose construction has been described in Vol. I., pp. 50–52, 1·2 tons of blende are roasted in 24 hours, from 30 per cent of sulphur down to 8 per cent., calcined ore being drawn four times This ore is then ground and calcined in reverberatory furnaces down to 1 per cent. of sulphur.

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[1] *Berg. und Hütten. Ztg.*, 1872, pp. 53—61.

Pyrites burners are low-shaft furnaces in which the ores to be roasted lie upon a grate of movable bars. These have been described and illustrated in Vol. I, p. 45 *et seq.* They are suitable for the preliminary calcination of easily combustible blendes, and will treat smaller pieces (down to walnut size) than will kilns. The sulphur may be brought down to 6 to 8 per cent. At Letmathe, near Iserlohn,[2] pyrites burners, 6 feet 3 inches to 6 feet 6 inches in length and width, and 4 feet 3 inches to 4 feet 5 inches high, each with one working door in both free sides, were employed, several such furnaces being built together in a block. Each shaft roasted 1 ton of zinc blende in 24 hours down to 7 per cent. of sulphur. The roasted ore was then roasted dead in reverberatory furnaces.

At Lipine, pyrites burners are at present (1895) in use, whose height above the floor of the works is 9 feet 2 inches; the shaft is 4 feet 1 inch square. Twenty-six furnaces form a block. The height of the layer of blende above the grate amounts to 16 inches. In 24 hours half a ton of blende, containing 25 per cent. of sulphur, is roasted down to 10 per cent. The gases evolved contain 6 per cent. by volume of sulphur dioxide. One attendant is required to every 10 furnaces, working a 12-hour shift. The roasted blende is crushed in rolls and then roasted dead in reverberatory furnaces.

At the Recke Works, near Rosdzin, in Upper Silesia, there are at present (1895) pyrites burners in use, the shaft being 3 feet 3 inches wide and deep, with a total height of 8 feet 2 inches. The blende is broken to nut size, and contains 24 to 33 per cent. of sulphur. The height of the layer above the grate amounts to 2 feet. In 24 hours, 7 cwts. of blende are roasted in each shaft down to 7 per cent. of sulphur; the escaping gases contain 7 per cent. by volume of sulphur dioxide. There are 23 to 30 such shafts combined to form one block; each such block requires two attendants with two assistants per day. The calcined ore is ground between rolls and then roasted dead in long-bedded calciners. The output of a set of rolls is 100 tons in 12 hours.

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[1] Vol. I., p. 49.

[2] Kerl, *Metallhüttenkunde*, p. 439.

Calcination of Crushed Blende in Shaft Furnaces

As far as the author knows, Gerstenhöfer furnaces are the only ones of this class that have come into use up to the present for calcining pulverulent blende These furnaces, which are specially adapted for pyritic blende, have been described and illustrated in Vol. I., p. 52. If the result is to be satisfactory, the blende must be crushed very small, entailing, however, the objection of the formation of a considerable quantity of flue-dust. Even in the most favourable conditions, the sulphur can nevertheless not be brought down below 5 or 6 per cent., so that even here a subsequent calcination in reverberatory furnaces is necessary; the Gerstenhofer furnace can also be used for this after-calcination by converting the lower part of it into a kind of reverberatory furnace by means of a lateral fireplace. In this case the escaping gases cannot be utilised in the manufacture of sulphuric acid, so that the employment of a long-bedded furnace for the dead roasting of the blende is preferable; the arrangement of a Gerstenhöfer furnace combined with an auxiliary fireplace is shown in Fig. 11. *T* is the lower part of the shaft with the carriers *t* for the ore; *F* is the firegrate from which the products of combustion pass through the flue *c* into the shaft. *H* is a portion of the dust chamber; *s* is a screw for the conveyance of the calcined ore into the wagon *w*; *k* is a flue which conveys the sulphur dioxide escaping from the residues into the stack. In the Gerstenhofer furnace 1 to 2 tons of blende can be roasted in 24 hours. It has the objection that a very considerable amount of flue-dust is produced, and for this reason has only been definitely employed in a small number of works. It has been used for calcining blende at the Mulden works, near Freiburg, and at Swansea, in England.

Calcination in Reverberatory Furnaces

Reverberatory furnaces should as a rule be employed for the calcination of zinc blende when the gases produced are not to be utilised. In highly cultivated countries the sulphur dioxide formed in these furnaces can only be allowed to escape into the air in a highly dilute condition, or else it has first to be rendered innocuous. Reverberatory furnaces admit of a rapid and complete calcination, and require less fuel and labour than muffle furnaces. The rabbling and stirring of the crushed ore requisite for a good calcination may be performed either by hand-work or mechanically. The working chamber of the reverberatory furnace is either fixed or else movable.

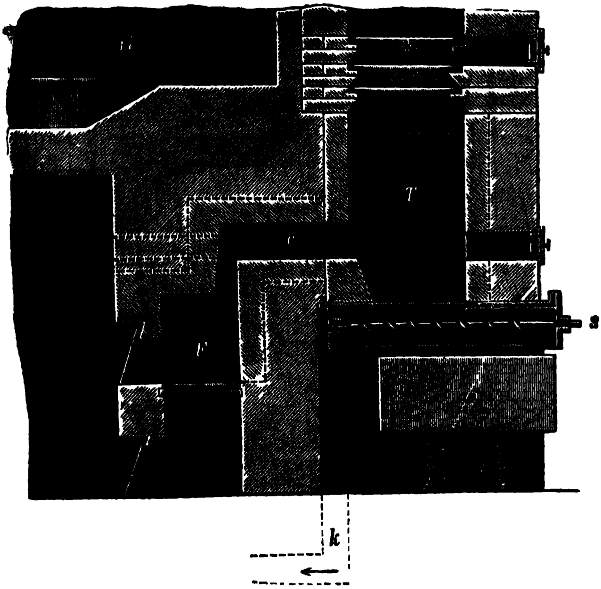

Fig. 11.

In the latter case, the hearth alone may either be rotated or else the whole working chamber may be movable. We therefore have to distinguish between—

Fixed Reverberatory Furnaces.

Reverberatory Furnaces with movable Hearths.

Reverberatory Furnaces with movable Working Chambers (rotating cylinders).

Calcination in Fixed Reverberatory Furnaces

Of the fixed reverberatory furnaces, only the ordinary reverberatory has up to the present come into use. Grate-fired shaft furnaces have not yet been used for the calcination of zinc blende. Whether the Stetefeldt furnace, which has given such excellent results as regards fuel consumption, labour, and output, in the chloridising roasting of silver ores (Vol. I, page 685), might not be suitable also for the oxidising roasting of zinc blende has not yet been proved experimentally. Fixed reverberatory furnaces may be divided into those worked by hand and those worked by machinery. The latter kind should be employed in districts where labour is high, whereas where labour is cheap the former class should have the preference both over the latter types, as also over reverberatory furnaces with movable hearths or working chambers.

Calcination in Fixed Reverberatories worked by Hand

It is only in rare cases that such furnaces are heated by the waste heat from zinc reduction furnaces. Such an employment of waste heat cannot be recommended, seeing how much care is required in the calcination of zinc blende, and seeing that the temperature which the various stages of this roasting require has to be carefully graduated. As a rule, therefore, the calcination of zinc blende should be carried on independently of the reduction furnaces.

Independent Reverberatory Furnaces worked by Hand

These furnaces are best built as long-bedded furnaces working continuously (*Fortschaufelungsöfen*). Such furnaces are best fitted with only one hearth, these presenting the advantages, as compared to those with several hearths one above the other, of smaller first cost, smaller need for repairs, and greater facility in working and charging; the latter kind should only be used where ground space is either very valuable or not obtainable. The heat economised by several hearths is not of any importance. It may also be saved with furnaces having but one hearth, if the products of combustion are carried off through arched flues disposed under the hearth, and if the furnace itself is coated with a nonconductor of heat. In spite of the above objections furnaces with two hearths have up to the present received the preference over those with one hearth. The length of the hearth depends upon the sulphur contents of the blende. As the sulphur acts as fuel, the hearth may be longer the greater the percentage of sulphur in the blende. Experience has shown that with single-hearth furnaces the hearth should not exceed 40 feet, and that with two hearths placed one above the other, the sum of the two hearths should not be greater than 50 feet. A greater length than the above is not beneficial as regards the result of the calcination, increases the first cost, and requires more labour. The width of the hearth must be such that the ore can readily be rabbled and pushed on. If the furnace only possesses working doors in one of its long sides, which seems to be an advantage in the calcination of blende in order not to dissipate heat, its width must not greatly exceed 8 feet. If, on the contrary, it has working doors on both of its long sides, the width of the hearth may be increased up to 13 feet. Such furnaces are however, only employed exceptionally, because a uniform calcination is more difficult in them, and the consumption of fuel is increased. The number of working doors must be kept as low as possible, as the furnace is cooled by them. In order to economise heat, it is therefore usual to have the working doors in one side only, in spite of the greater difficulties in working. Experience has shown that the distance between the centre lines of two adjacent working doors should not exceed 8 feet, for the sake of convenience in working. The projections between the working doors must also be kept as small as possible. The distance between the hearth and the arch of the roof should not greatly exceed 18 inches. To utilise the heat to the best advantage, it is usual to incline the arch of the roof downwards, or to allow the hearth to rise either uniformly or stepwise, towards the flue-bridge. As very high temperatures are not required for calcination, an ordinary grate-fire is generally employed; gas-firing is only made use of when inferior fuels, or fuel that will not give a long flame, are alone available. The construction of such a long-bedded calciner for the calcination of zinc blende does not differ, except as regards dimensions, from the furnace described and illustrated in Vol. I., p. 68. In a single-hearth calciner 40 feet in length, 8 to 10 feet wide, with a grate 6 feet 6 inches long and 18 inches wide, 3 tons of zinc blende can be roasted in 24 hours with a consumption of 1 ton of coals, and with one man per shift.[1] The ore is introduced in charges of 15 cwts. through an opening in the roof of the flue, and is pushed forward at intervals of 6 hours. Accordingly, there are four charges of ore in the furnace at once, and 15 cwts. are drawn every 6 hours. The ore is rabbled in 15-minute intervals.

Long-bedded calciners with several hearths usually possess two of the latter; more than two are only used exceptionally. The construction of such a double-hearth furnace is shown in Figs. 12 and 13.[2] Four such furnaces are built together to form a block; *c* is the grate, lying 2 feet 4 inches below the fire-bridge *d*, which is hollow and cooled by an air flue; *a* is the lower hearth, a_1 the upper hearth, the length of each being 15 feet 3 inches, and their clear width 8 feet; *e* is the flue through which the products of combustion escape into the condensing flues, e_1, and thence to the flue *f*, leading to the stack. To each block of four furnaces there is one stack; *i* is the ashpit, *h*, *k* are the working doors, *g* is an opening closed during calcination, through which the calcined blende can be dropped into the vault. In such a furnace 3 to 4 tons of blende are roasted in 24 hours, with one man on each shift, and with a consumption of 30 per cent. of fuel. Double-bedded furnaces have been used at the zinc works in Upper Silesia, Westphalia and Belgium, and are still used where not replaced by muffle furnaces. In these from 2½ to 6 tons of ore, according to the size of the furnace, are put through, with a consumption of from 25 to 40 per cent. of coal, according to the quality. For the smaller furnaces treating up to 3 tons, one workman per shift is enough; for the larger furnaces two men are required.

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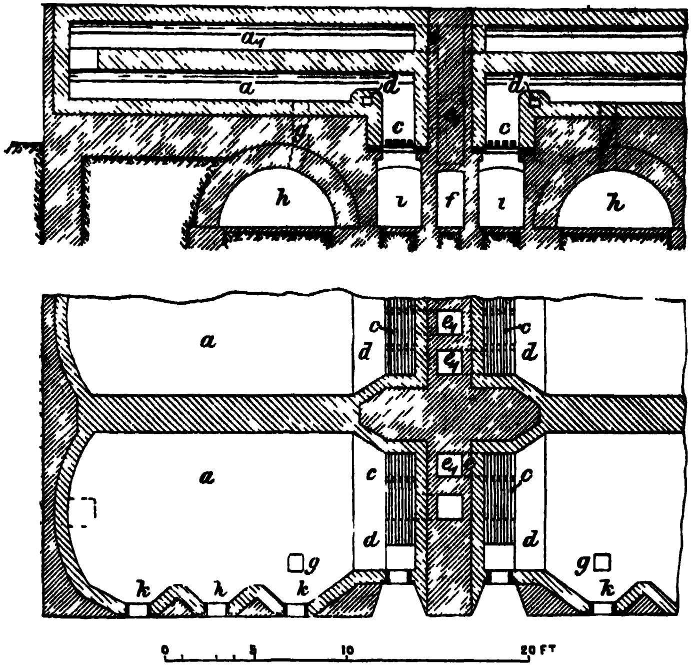
[1] Thum, *op. cit.*, p. 202.

[2] *Berg. und Hütten. Ztg.*, 1877, p. 100.



FIGS 12 and 13.

At Oberhausen[1] the furnace hearths are each 21 feet 4 inches long and 6 feet 6 inches wide. The cross section of the grate is 6 feet 6 inches by 1 foot 4 inches. In 24 hours, 3 tons of ore are put through, with a consumption of 12 to 14 cwts. of small bituminous coal, containing 11 per cent. of ash. The calcined ores contain 0·57 to 0·83 per cent. of sulphur. The loss of zinc during calcination does not exceed 0·75 per cent. At Ammeberg,[2] in Sweden, similarly constructed furnaces are used, fired by gas. In 24 hours, 3 tons 2 cwts. of blende are calcined down to 1·20 to 1·25 per cent. of sulphur, with a consumption of 11 cwts. of small coal. Four furnaces are worked by a staff of 20 men in two 12-hour shifts. At Münsterbusch, near Stahlberg, a furnace with hearths 20 feet 7 inches in length and 9 feet 3 inches in width, having 5 working doors along one side, calcined 2½ tons of blende per 24 hours in 4 charges, with a consumption of 39 cubic feet of coal. Every 6 hours a charge of ore was drawn from the furnace, and a new charge put in. Three hours after each charging, all the ore contained in the furnace was thoroughly rabbled. At the Hohenlohe Works, near Kattowitz, in Upper Silesia, there are double-bedded furnaces, with 5 working doors along one of the longer sides. Three charges of 1 ton each are contained simultaneously in the furnace, two on the upper and one on the lower hearth. Each charge remains for 5 hours before it is moved forward, so that the ore remains altogether 15 hours in the furnace. Every 5 hours a charge is drawn from the furnace, and a new charge introduced upon the upper hearth. In 24 hours some 5 tons of blende are calcined down to 1 per cent. of sulphur in one such furnace, with a fuel consumption amounting to 25 per cent. of the weight of the raw ore. The escaping gases contain 1 per cent. by volume of sulphur dioxide. For the absorption of the latter they are made to pass upwards and downwards through towers containing milk of lime, and finally discharged into a stack 328 feet high. At the Silesian Works, near Lipine, double hearth calciners are at present (1895) in use. The length of the hearths amounts to 22 feet, the width to 6 feet 6 inches, There are 4 to 5 working doors to each hearth. The furnace contains 3 charges of 13 cwts. each at one time. In 24 hours a furnace puts through 5 tons 2 cwts. of blende, with a consumption of 24 cwts. of inferior coal. The labour employed in the 12-hour shift amounts to 2¼ men, two of whom look after the calcining and the firing; a labourer, working a quarter shift, looks to the charging of the blende and wheels in the coals. At the Recke works, near Rosdzin, double-hearth calciners are at present (1895) in use, the length of each hearth being 20 feet. The width amounts to 6 feet 6 inches, with six working doors to each hearth. In 24 hours, 3½ tons of blende are calcined, with a consumption of 1 ton of small coal. One man works the furnace on a 12-hour shift. At the Cilli[1] works a part of the blende, poor in sulphur, is calcined in double-hearth furnaces, each hearth being 25 feet long and 8 feet broad, with working doors along one of the longer sides. In 24 hours 3 charges of 15 cwts. each are roasted.

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[1] Mahler, *Annales des Mines*, Vol. vii., book iii., p. 152, 1885.

[2] *Ibid.*

The decrease in the sulphur and the formation of zinc sulphate during the calcination of blende in a double-bedded calciner at the works of the Vieille Montagne, near Flône, in Belgium, are shown in the following table, in which A designates uncalcined ore, Z calcined ore, 2 to 8 the various samples taken one after another :—

Sample.	Zinc Sulphide per cent	Zinc Sulphate per cent.	Zinc Oxide per cent.
A	83·0	0	0
2 . .	70·5	3·7	15·2
3 . .	52·2	3·9	34·6
4 .	51·5	4·2	38·0
5 . .	43·0	11·0	41·5
6 .	23·2	12·3	57·8
7 . .	17·7	7·8	65·0
8 . .	8·6	6·2	75·5
Z	1·9	5·9	81·0

A similar comparison of the results of calcining blende in a single-hearth reverberatory furnace at the works of the Austro-Belgian Company at Corphalie, in Belgium, is as follows :—

Sample.	Zinc Sulphide per cent	Zinc Sulphate per cent	Zinc Oxide per cent.
A .	64·5	0	0
2 .	58·0	3·4	4·6
3 . .	38·0	7·9	19·0
4 . .	17·5	8·4	39·0
5	10·0	2·6	50·5
Z . . .	1·2	2·2	59·7

Multiple-hearth furnaces are used at La Salle in the State of Illinois, United States of America.[2] The separate hearths form shelves placed alternately one above the other, as in the Maletra furnace (Vol. I., page 58), over which the ore passes from top to bottom, whilst the flames and products of combustion travel in the opposite direction. The furnace forms a cube of 15 feet side and is composed of 5 separate divisions lying side by side, each 3 feet wide and 15 feet long. Each of these divisions has 8 hearths one above the other, as described. Each furnace of 5 compartments puts through 36 cwts. of blende in 24 hours. Recently the muffle furnaces, hereafter to be described, have been employed at La Salle.

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[1] *Berg. u. Hütt. Ztg.*, *No.* 4, 1894.

[2] Leob, *Jahrb.*, vol. xxvii., p. 316, 1879.

Reverberatory Furnaces heated by the Waste Heat of Zinc Reduction Furnaces and worked by Hand

Such furnaces have been constructed by Thum in England, where they were heated by the waste heat of a Belgian zinc furnace. Such a furnace with a hearth 41 feet long and 10 feet broad, the height of the arch above the hearth being 2 feet, is in operation at Bagillt, and calcines 30 to 32 cwts. of blende in 24 hours. These furnaces are open to the serious objection that the calcination is entirely dependent upon the working of the reduction furnaces, and are therefore not to be recommended. Waste heat from the reduction furnace can be employed more advantageously for other purposes.

Calcination in Fixed Reverberatory Furnaces worked by Machinery

The furnaces belonging to this class are furnaces with movable rabbles for stirring the blende. On account of the high temperature which the calcination of blende requires in its later stages, it is advisable only to employ these mechanically moved rabbles in the first portion of the calcination, that is to say, on the upper hearths, and to complete the dead-roasting by hand; as the movable portions are continually in need of repair and occasion no inconsiderable expense, such furnaces can only be employed with advantage in districts where wages are high. In spite of their economy in labour, they have up to the present been employed in but few works. Experimentally, a furnace of this kind—that of Ross and Welter—was employed at Oberhausen.[1] This furnace consists of 3 hearths, one above the other, of which the lowest is straight like that of a long-bedded calciner, whilst the two upper hearths are circular; in the two upper hearths rabble-arms, attached to a vertical shaft, are rotated as in Parkes's furnace (Vol. I., page 78). There is a charging apparatus which delivers the ore to the topmost hearth, and by means of the revolving rabbles, which make one revolution per minute, it is stirred and gradually transferred to the lower hearth. It is here again stirred by the rabble revolving once per minute and gradually pushed on to the bottom hearth, where it is rabbled and advanced by hand. The rabbles are secured to a sleeve, through which passes a vertical hollow cast-iron shaft. The latter is moved by gearing, and thus sets the sleeve in motion; air is made to pass through the hollow shaft in order to cool it. In this furnace, which is worked by one man, 3 tons of blende are said to be put through in 24 hours, with a consumption of 15 cwts. of coal.

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[1] Mahler, *Berg. und Hütten. Ztg.*, p. 180, 1886.

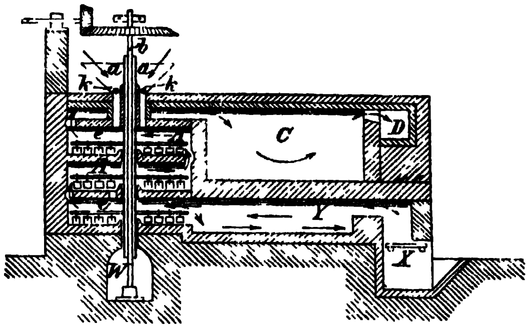

FIG. 14

This furnace would appear to be identical with one patented by the Vieille Montagne Company,[1] except that the latter has three round hearths. The construction of the patented furnace is shown in Fig. 14. *A*, *A* are the three round hearths situated one below the other, *Y* is the rectangular hearth, *X* is the fire-grate. The products of combustion first pass over the hearth *Y*, and then over the round hearths one after the other, as shown in the figure by the arrows. From the topmost hearths they pass to the dust chamber *C*, and from the latter to the flue *D*. The ore is charged by means of a hopper *a*, and delivered by means of grooved rollers on to the topmost hearth of the furnace, whence it is gradually transferred by means of the rabbles to the lower hearths, and ultimately on to the rectangular hearth, where it is worked by hand, and finally drawn off in the calcined state. The shaft *b* of the rabbles is surrounded by a cast-iron cylinder, which is so attached to the shaft that it rotates with it; air enters the hollow space between the shaft and the cylinder from the flue *W*, in order to cool the shaft, and escapes at its upper portion situated outside the furnace.

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[1] German Patent, No. 24,155.

A hollow shaft could also be employed (as in the furnace of Ross and Welter), the rabble arms being attached to a sleeve consisting of two halves; this sleeve is secured to the shaft or to the cast-iron cylinder. On each bed there are two rabble-arms, *e*, secured to the shaft; the one is provided with tines placed radially, whilst inclined blades are attached to the other. The teeth rabble the ore, whilst the inclined blades of the other arms push it according to their direction, either towards the middle or towards the circumference of the hearth, where it passes through suitably disposed openings on to the hearth below.

At Oberhausen there are at present in use muffle furnaces with movable rabbles.

Another form of reverberatory furnace worked by machinery (that of O'Harra, Vol. I., page 72) which is distinguished by its great capacity and its small consumption of fuel, has hitherto only been employed for the calcining of copper ores and lead ores. It should, however, also be suitable for a preliminary roasting of zinc blende, just like the upper hearths of a multiple-bedded reverberatory. The dead-roasting of the blende would in that case be completed in a separate furnace, worked by hand. Other furnaces which should be suitable for the calcination of zinc blende under the above conditions are the Turret furnace of Pearce (Vol. I., page 75), notable for its large output, as also the very efficient horse-shoe furnace of Brown (Vol. I., page 76). The latter is especially recommended as requiring very few repairs. It is used for the calcination of blende at the works of the Collinsville Zinc Company of Collinsville, Illinois, U.S.A., and at the Glendale Zinc Works of South St. Louis, Missouri, where it has given good results. At the Collinsville works, one furnace with 4 grates produced 10 tons of roasted blende with 0·85 to 1 per cent. of sulphur in 24 hours from ore containing originally 30 per cent. of sulphur. The consumption of fuel, 6 tons of duff in 24 hours, must not be taken as a standard, on account of the inferior quality of the coal.

Calcination in Reverberatory Furnaces with Movable Hearths

Reverberatory furnaces with movable hearths have only been used exceptionally on account of their high consumption of fuel and their comparatively small output compared with that of fixed furnaces; and on account of these objections, as also on account of the high temperature required for calcining blende, they are not likely to come into extensive use. Up to the present, they have only been employed with advantage for the chloridising roasting of copper ores, for which process a very low temperature is required (see Gibbs and Gelstharpe furnace, Vol. I., page 230), as also for the calcination of tin ores containing arsenical pyrites, which likewise does not require a high temperature (Brunton furnace, see under Tin), and then only in districts where the cost of labour is high.

Kuschel and Hinterhuber have designed a furnace which has been used at Johannisthal in Lower Carinthia.[1] This furnace is provided with a round hearth capable of revolving, and with rabble-teeth of firebrick, which pass through the roof of the furnace, and can be withdrawn from the rabble arm, but are fixed during the progress of the calcination. There are two rabble arms, each with 5 teeth. These teeth are so arranged that as the hearth revolves, those in one arm occupy the position of the furrows produced by those in the other arm. These teeth are hollow, and also serve for the introduction of the powdered ore into the furnace. When the oven is to be charged, the upper portions of the teeth are open, these being closed during the progress of the operation by clay plugs. The latter are lifted, and by means of a funnel powdered ore is introduced into the hollow teeth. By the slow turning of the hearth the ore then becomes distributed over it. When the furnace is to be emptied, a grating formed of inclined iron plates, which is concealed in a radial slot in the furnace arch when not in use, is let down upon the hearth, as in the case of the Gibbs and Gelstharpe furnace, and by this means the calcined ore is pushed into four apertures at the edge of the hearth, and thênce into a vault beneath the furnace. The diameter of the hearth is 13 feet, the height at the centre is 20 inches, and at the circumference 7 inches; the arch is 12 inches in thickness. The furnace is fired by means of 2 grates lying side by side, the products of combustion escaping through 13 flues opposite to the fireplace. In order to promote calcination, water vapour is injected in the last stages. In 24 hours 1 to 2 tons of blende are said to be roasted in this furnace, with a consumption of 1·2 tons of coals. The roasting is said not to be as complete as might be desired. On account of the above-named objections, this furnace has not come into general use.

Calcination in Reverberatory Furnaces with Movable Working Chambers

These furnaces are composed of rotating cylinders working intermittently or continuously, and have up to the present been used with great advantage for the oxidising roasting of copper ores and for the chloridising roasting of silver ores, in districts where wages are high. As far as is known to the author, they have not been used for calcining zinc blende, though there is no doubt that zinc blende could be calcined in such furnaces. Considering the long time which the complete calcination of blende requires, and the high temperature requisite in the last stage, continuous-acting furnaces should be more satisfactory than those that work intermittently. As it is doubtful whether calcination could be completed in one of these cylinders, it *might, in case of necessity, be requisite to combine several of these* furnaces, one after the other. Their use would only be indicated in districts where wages are very high.

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[1] *Berg. und Hütten. Ztg.*, 1871, p. 321; 1872, p. 200.

THE NEUTRALISATION OF THE ACIDS OF SULPHUR EVOLVED BY CALCINATION IN REVERBERATORY FURNACES

When zinc blende is roasted in reverberatory furnaces, whether it has undergone a previous preliminary roasting or not, the neutralisation of the products of calcination, containing sulphur dioxide, together with a small quantity of sulphur trioxide, plays a very important part; it is only in countries which are as yet sparsely cultivated, and in districts in which vegetation has already been destroyed by the effect of these gases, that the latter may be evolved direct into the atmosphere in their concentrated form; in all other places they must be neutralised. For example, in Prussia, the main seat of the production of zinc, such gases may only be allowed to escape into the air when their contents of sulphur dioxide are so small that no injurious action upon the vegetation is to be feared. The best and most profitable method of neutralisation of these gases, viz., the conversion of sulphur dioxide into sulphuric acid, cannot be applied to the gases evolved from reverberatory furnaces, because the sulphur dioxide escapes from it in a condition of such excessive dilution (less than 2 per cent. by volume), and because it is intermixed with the products of combustion of ordinary fuel, which have an injurious effect upon the nitrous gases in the manufacture of sulphuric acid. For this reason reverberatory furnaces are especially used for calcining blende in those cases in which the utilisation of sulphur dioxide for the manufacture of sulphuric acid is impossible, owing to the absence of any market for the latter. The processes, by which the products of combustion containing sulphur dioxide can be neutralised, only exceptionally admit of the latter being utilised at the same time. As a rule, these operations increase markedly the cost of calcination. All attempts up to the present not only to neutralise but at the same time to utilise the gases from reverberatory furnaces have remained fruitless, because they have been found to be too costly; there is here, therefore, a wide field open to metallurgical discovery. Sulphur dioxide has been rendered innocuous by diluting the gases containing it with air, or by absorbing it by means of water, of sulphuric acid of 50° B., of milk of lime, of limestone and water, of oxide of zinc, of basic zinc carbonate, of magnesia, of ferric oxide, of ferric sulphate, of solution of sodium sulphide, of calcium sulphide, or of iron kept moist, and by conveying it into waste heaps of alum ores.

The dilution of sulphur dioxide by means of air can be performed by allowing the products of calcination to escape from the furnaces into the upper regions of the atmosphere by means of high stacks. The sulphur dioxide thus produced diffuses through extensive layers of air, and is diluted by these to such an extent that, on its descent, it no longer has an injurious effect upon vegetation. This dilution of sulphur dioxide can only, however, be attained when the quantities of blende to be roasted are limited and therefore only inconsiderable amounts of gases are evolved, as otherwise the injurious effect of these gases becomes noticeable in time in a wide area surrounding the calcining works. If the contour of the country admits of it, such stacks should be situated on the tops of high hills and connected with the furnaces by means of inclined flues. The height of these stacks varies with their position between 330 and 500 feet (at Hamborn 333 feet, at Freiberg 466 feet). As the draught of a stack cannot be increased by increasing its height above 160 feet, all prime costs which are necessitated by the construction of a stack higher than this must be charged to the neutralisation of the sulphur dioxide.

These first costs are very considerable, but only result in a small working charge, because the actual neutralisation of the sulphur dioxide then costs nothing. If, therefore, comparatively small quantities of these gases have to be liberated, the best method of rendering them innocuous is by means of such high stacks.

The products of calcination can only be imperfectly neutralised by the help of water, because water either falling in the form of rain or trickling through a coke tower absorbs only comparatively little sulphur dioxide from diluted gases, and scarcely any from hot gases. The experiments which have been tried to remove sulphur dioxide from the gases given off from a reverberatory furnace by means of lead towers filled with coke, over which water trickles, were not only unfavourable as regards the absorption of the sulphur dioxide, but also required towers of large area, together with powerful fans, in order to maintain the draught, suitable dust chambers, and the previous cooling of the gases. The method of absorbing the sulphur dioxide by means of water has therefore not come into use. The absorption of sulphur dioxide from the products of combustion by means of sulphuric acid at 50° B, which was attempted with the blende calcining furnaces of the chemical factory at Rhenania, near Stolberg, has also been found imperfect, because the sulphuric acid, whilst it readily absorbed the sulphur trioxide contained in small quantity in these gases, did not absorb the sulphur dioxide. The plant employed was a tower filled with coke over which the sulphuric acid was allowed to trickle. Apart from the imperfect absorption of the sulphur dioxide, the same objections arose as in the case of absorption by water. This method, therefore, has found no further application.

Sulphur dioxide and sulphur trioxide are readily absorbed by milk of lime, calcium sulphite and sulphate being produced. The former is gradually converted on contact with air into the latter salt. The product of the absorption is therefore a mixture of calcium sulphite and sulphate, which, as experiments at the Hohenlohe Works, near Kattowitz, in Upper Silesia, have shown, may be used either as a disinfectant, as a vermin destroyer, or as manure when mixed in certain proportions with animal manure, or in the case of well-manured ground rich in humus, even without such admixture. The quantities of this salt for which a market can be found are, however, so small compared with the great quantities in which it is produced that it is not only worthless, but may even be looked upon as a waste product occupying much space and therefore troublesome.

The absorption of the sulphur dioxide takes place in accordance with the following equation:—

$$CaH_2O_2 + H_2SO_3 = CaSO_3 + 2H_2O.$$

It takes place on contact and requires an excess of the absorbing solution in order to be complete. The absorption is therefore carried out by exposing the gases in towers to a rain of milk of lime, and again using the product thus obtained, which still contains a considerable quantity of free calcium hydrate, as an absorbent. The composition of the salt is as follows, according to Dr. Grosser of Kattowitz:—

CaO	37·75
MgO	1·45
Al_2O_3	4·14
Fe_2O_3	1·10
SO_2	38·40
SO_3	2·85
CO_2	4·15
Soluble SiO_2 and residue	5·53
H_2O	3·40
	98·77

According to this composition, the contents of calcium sulphite amount to 72 per cent., and of calcium sulphate to 4·84 per cent. Upon the average the salt, as produced at the Hohenlohe Works, contains about 34 per cent. of SO_2 and 5 per cent. of SO_3, equivalent to 64 per cent. of calcium sulphite and 8·5 per cent. of calcium sulphate, together with 6 to 10 per cent. of water.[1] The absorption of sulphur dioxide by milk of lime is made use of in several of the large works in Upper Silesia, but is carried out on the largest scale at the above-mentioned Hohenlohe Works. At these works the products of combustion are drawn by means of stacks upwards and downwards through towers down which milk of lime is trickling, and escape, containing only very small quantities of sulphur dioxide, into a stack 328 feet high, by which the last remaining portions of sulphur dioxide are carried into such a high stratum of the atmosphere that they no longer exert any injurious action. The solution trickling down the towers is led into sumps in which the salt is deposited. It is lifted out from these mechanically and piled in heaps, whilst the clear solution is used again for dissolving fresh portions of gas. Although the process is expensive, yet it completely fulfils its purpose, and has up to the present not been replaced by any other method.

The sulphur dioxide of the gases escaping from reverberatory furnaces can also be neutralised by means of water and limestone or dolomite. For this purpose towers are filled with fragments of the above-mentioned substances and water is allowed to trickle through them. The sulphur dioxide in the gases passing up these towers form calcium or magnesium sulphite. The absorption in this method is less energetic than it is by milk of lime, and requires towers of large area, considerable quantities of fluid, and a good draught. It has therefore, not yet come into use at zinc works.

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[1] Kosmann, *Oberschlesien*, etc., p. 199.

Zinc oxide, basic zinc sulphate and magnesia have only been used experimentally for neutralising the sulphur dioxide from blende calcining furnaces. These bodies form sulphites of zinc or magnesia, which are readily decomposed on heating, with the evolution of *concentrated sulphur dioxide. By their use, therefore, the diluted sulphur dioxide of the gases escaping from the furnaces can be con* centrated, whilst the absorbent is regenerated. These sulphites by long exposure to the air and moisture can also be converted into sulphates. As, however, before sulphur dioxide could be absorbed the gases had previously to be cooled down, and as flue-dust had also to be removed from them; as moreover during their absorption a considerable quantity of sulphates was formed, together with sulphites, which former salts are only imperfectly decomposed when the mixture is heated for the production of concentrated sulphur dioxide, the neutralisation of furnace gases by means of the substances in question has not come into extended use. Experiments to convert the dilute sulphur dioxide of the furnace gases into concentrated sulphur dioxide by means of water have failed on account of the low absorbing power of water upon dilute sulphur dioxide. The object of the experiments was to absorb sulphur dioxide by means of water and then to evolve it in a concentrated form by heating the solution. This process, which will be explained more fully further on, is only available when the gases contain at least 4 per cent. by volume of sulphur dioxide.

Moist ferric oxide absorbs sulphur dioxide slowly with the formation of ferrous and ferric sulphates. Ferric sulphate absorbs it with the formation of ferrous sulphate. On account of the slow rate of absorption and the low value of the products, neither of these methods have come into use. All attempts to produce sulphur by the reduction of the furnace gases by the aid of carbon have given most unsatisfactory results. Still less satisfactory were the experiments to separate sulphur by the action of sulphuretted hydrogen upon the dilute gases. A solution of sodium sulphide absorbs sulphur dioxide well, with the formation of sodium sulphate and sulphur, but has been found to be too expensive in practice. Solutions of polysulphides of calcium absorb the sulphur dioxide of furnace gases readily with the production of sulphur, but come too expensive. Calcium monosulphide cannot be used as an absorbent on account of its low solubility in water.

Kosmann[1] has proposed to convert calcium monosulphide by treating it with carbon dioxide and water into calcium sulph-hydrate, as is done by Chance in his process for treating the residues from the manufacture of soda by the Leblanc process, for the production of sulphuretted hydrogen or sulphur, and to use this calcium sulph-hydrate as an absorbent for the sulphur dioxide of the furnace gases. The oxides of sulphur are absorbed by calcium sulph-hydrate with the formation of calcium sulphite or sulphate, sulphur separating out as is shown by the following equation :—

$$CaH_2S_2 + 2H_2SO_3 = CaSO_3 + 3S + 3H_2O.$$

A precipitate of calcium sulphite and sulphate and of sulphur is thus obtained.

By the action of carbon dioxide upon calcium sulphite, calcium sulph-hydrate and calcium carbonate are first formed. On further action the calcium sulph-hydrate is decomposed with the evolution of sulphuretted hydrogen, calcium carbonate being produced :—

$$3CaS + H_2CO_3 = CaCO_3 + CaH_2S_2 + CaS.$$
$$CaH_2S_2 + H_2CO_3 = CaCO_3 + 2H_2S.$$

Kosmann interrupts the process when the greater proportion of the calcium sulphide has been converted into sulph-hydrate, and conducts the sulphuretted hydrogen produced into a further quantity of monosulphide, which is also converted into sulph-hydrate by the sulphuretted hydrogen. According to Kosmann the equations are as follows :—

$$3CaS + H_2CO_3 = CaCO_3 + CaH_2S_2 + CaS.$$
$$CaH_2S_2 + CaS + H_2CO_3 = CaCO_3 + CaH_2S_2 + H_2S.$$
$$CaS + H_2S = CaH_2S_2.$$

Thus four molecules of calcium sulphide and two of carbon dioxide produce two molecules of calcium sulph-hydrate and two of carbonate, or two molecules of calcium sulphide yield one molecule of calcium sulph-hydrate. The solution of calcium sulph-hydrate is blown by means of an injector into the furnace gases, together with water vapour. The sulphur dioxide is then absorbed, as is shown by the following equations :—

$$CaH_2S_2 + H_2SO_3 = CaSO_3 + 2H_2S.$$
$$2H_2S + H_2SO_3 = 3S + 3H_2O.$$

Each molecule of sulph-hydrate therefore absorbs two molecules of sulphur dioxide with the formation of one molecule of calcium sulphite or sulphate and the production of three atoms of sulphur. As two molecules of calcium sulphide are required for the formation of one molecule of sulph-hydrate if the process were conducted exactly in accordance with the theory, each molecule of calcium sulphide would neutralise one molecule of sulphur dioxide, and at the same time separate 1½ atoms of sulphur. The sulphur is obtained mixed with calcium sulphite or sulphate. It is removed from this mixture by boiling with caustic lime, whereby calcium polysulphide is produced, the latter being employed as an absorbent for the sulphur dioxide. The greater portion of the sulphur is thereby precipitated with the simultaneous formation of calcium sulphite and sulphate. From the precipitate so obtained the sulphur may be recovered by distillation. The process, though theoretically sound, has not yet come into practical use. Although calcium sulph-hydrate and calcium polysulphide absorb sulphur dioxide far better than does milk of lime, it must nevertheless be borne in mind that the production of the carbon dioxide required for the process by the burning of limestone or the combustion of coke entails no inconsiderable cost; that the calcium carbonate produced when the sulph-hydrate is formed cannot be utilised, and thus constitutes a troublesome substance occupying a great deal of space; that the preparation of calcium sulphide by the reduction of calcium sulphate, whenever this cannot be obtained in the form of residues from the Leblanc process, also entails expense; and that of the calcium contained in it, only half can be converted into sulphate or sulphite, whilst the other half is converted into carbonate. From the sulphate or sulphite calcium sulphide can be regenerated, but not from the carbonate. For the production of the requisite calcium sulphide it is therefore necessary to add calcium sulphate to the extent of one-half of that entering into the process. Finally, considerably more sulph-hydrate is required than theoretical calculation would indicate, because the furnace gases always contain oxygen and carbon dioxide, both of which act upon the sulph-hydrate, the former converting the sulph-hydrate partly into calcium hyposulphite and partly into calcium polysulphide in accordance with the equations:—

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[1] Gluckauf, *Berg. und Hütten. Ztg.*, in Essen, No. 35, May 2, 1894.

$$CaH_2S_2 + 4O = CaS_2O_3 + 4H_2O.$$
$$CaH_2S_2 + O = CaS_2 + H_2O.$$

Whilst calcium polysulphide absorbs sulphur dioxide, the hyposulphite is not affected by it. All the sulph-hydrate which is converted into that salt is therefore lost to the process. The calcium polysulphide produced is at the same time less effective as an absorbent than is the sulph-hydrate, seeing that two molecules of the former only absorb three molecules of sulphur dioxide, instead of four molecules, as in the latter case. Carbon dioxide attacks the sulph-hydrate with the formation of sulphur and calcium carbonate, so that this calcium takes no part in the absorption of sulphur dioxide.

Metallic iron moistened with water, as proposed by Winkler, acts well in the case of gases rich in sulphur dioxide, as, for example, those generated in the parting of gold by sulphuric acid, but it is less effective in the case of dilute gases, such as are thus evolved from the blende calcining furnaces. At Flône, in Belgium, the furnace gases have been passed into waste heaps of alum ores by which the latter were rendered soluble. The employment of this process is, however, only possible under very exceptional local conditions. Further information respecting experiments upon the neutralisation of sulphur dioxide will be found in the works of Reich, Freiberg 1858; Winkler, *Freiberger Jahrbuch*, 1880, p. 50; Schnabel, *Preuss. Zeitschr. f. Berg.-Hütt. u. Salinen-Wesen*, 1881, 29, p. 395; Hasenclever, *Fischer's Jahresberichte*, 1881, p. 173, 1886, p. 257; *Zeitsch. d. Ver. Deutsch. Ing.* 1886; C. A. Herring, *Die Verdichtung des Hüttenrauchs*, Stuttgart, 1888.

Calcination in Combined Reverberatory and Muffle Furnaces

These furnaces are only employed when a portion merely of the sulphur dioxide evolved on calcining blende is to be utilised in sulphuric acid manufacture, whilst the remainder is to be allowed to escape unused. In this case the sulphur dioxide developed in the muffle furnace is conveyed into lead chambers, whilst that escaping from the reverberatory furnace is either led direct into the air or previously neutralised. The principle of these furnaces is, that the muffles in which the first stage of the calcination of the blende is conducted shall be heated by the gases of the reverberatory furnace, in which the blende is roasted dead. The muffles may either lie partly inclined or else horizontally. The Hasenclever-Helbig furnace, designed in the year 1874 by Hasenclever and Helbig, and used with great advantage in the Rhine districts, Westphalia and Silesia, is a furnace with partly inclined muffle. At present it has been replaced at most works by the muffle furnace to be described further on, which admits of the complete utilisation of the sulphurous gases evolved in calcination. There are, however, still a few of these furnaces in operation at Lipine, which are shortly to be pulled down. The furnace consists, as shown in Figs. 23 and 24, of a muffle constructed in two parts, situated over a reverberatory furnace; the lower part of the muffle *m* is horizontal, whilst the upper part *n*, which adjoins it, lies at an angle of 43°. In the inclined portion walls of hard-burnt bricks

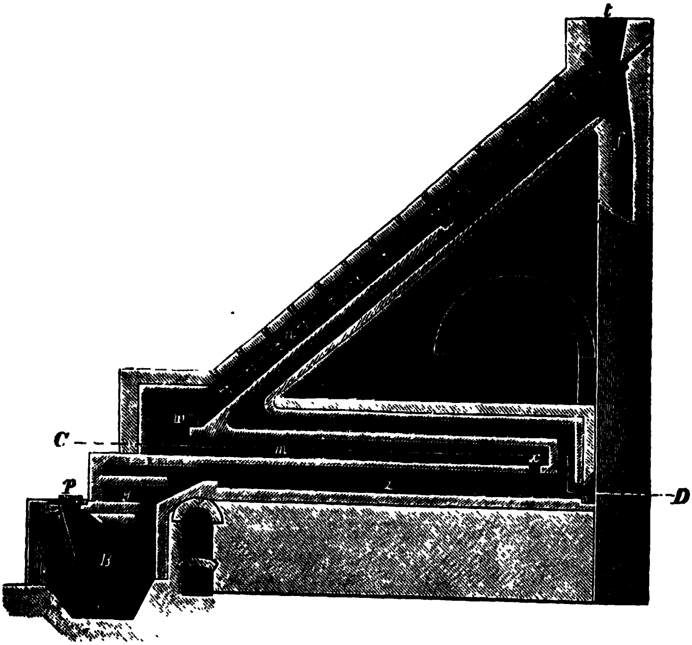

Fig. 23.

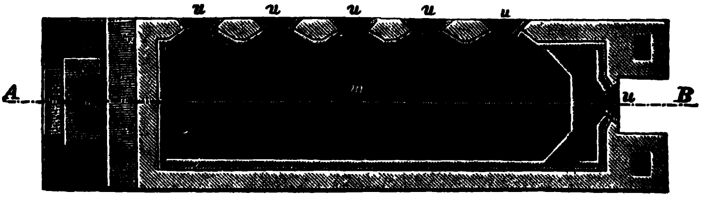

Fig. 24.

0 1 2 3 4 5 10 20 FT

are built some 20 inches apart, at right angles to the long axis of the muffle, and hang down so far that between their bottom edge and the floor of the muffle there is only a space of less than an inch. The object of these walls is to spread the ore, which is charged at the upper end of the muffle, in a thin bed upon the floor of the latter. In order to enable the products of combustion to pass unhindered by these partition walls, there are lateral openings in them, so that the gas escapes following a sinuous line alternately at one side or the other of the walls, as shown in Fig. 25. The pulverulent blende is charged from the hopper *t* at the upper end of the muffle, slides along the bottom of the latter, and at definite intervals of time—from 2 to 5 minutes—is carried by the roll *w* which is driven by a small water wheel, into the lower horizontal portion of the muffle, where it is spread out and further roasted. At the far end of the horizontal portion of the muffle there is an opening *x*, through which the blende is dropped into the working chamber *z* of the reverberatory furnace, where it is roasted dead. The products of combustion of the reverberatory furnace first heat the floor and then the arch of the horizontal portion of the muffle, and then rise up underneath the inclined portion of the latter into the flue *f*. The sulphurous gases evolved in the horizontal portion of the muffle pass into the inclined portion, where they unite with the gases evolved there, and together escape from the upper end of the muffle into a flue which conducts them to the sulphuric acid chambers. At the end of the muffle the blende will have lost 60 per cent. of its sulphur, still containing from 8 to 10 per cent., whilst the gases that escape from the muffle carry at least 6 per cent. by volume of sulphur dioxide, and are very suitable for sulphuric acid manufacture. The blende is then calcined down to 1 per cent. of sulphur upon the hearth of the reverberatory furnace, which forms a long-bedded calciner with working doors along one of its longer sides. The furnace may be fired either by a grate or by gas. In the figure it is shown as fired by gas, a Boëtius producer, *B*, being employed. The air, which is heated in the walls of the latter, enters at *y*; the fuel is charged at *p*. The temperature in the inclined portion of the muffle is as high as the melting point of antimony (432° C.). In this furnace 3 to 4 tons of zinc blende can be calcined down to 1 per cent. of sulphur in 24 hours, with a consumption of coal equal to 28 to 50 per cent. of the weight of the raw ore. At the Recke Works such a furnace was formerly in use calcining 3½ tons of blende down to 1 per cent. of sulphur in 24 hours, with a consumption of 2 tons of coal.[1]

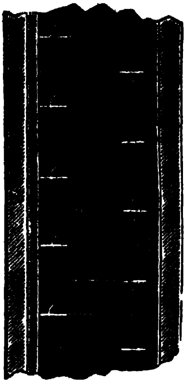

FIG. 25

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[1] *Berg. und Hutten. Ztg.*, 1877, p. 71.

At Oberhausen [1] the furnace had the following main dimensions: Cross section of the gas producer, 2 feet by 6 feet; floor of the horizontal portion of the muffle, 6 feet by 24 feet 7 inches; of the inclined portion of the muffle, 6 feet by 32 feet 10 inches; of the reverberatory furnace, 6 feet by 18 feet 8 inches. Of the sulphur contents of the blende 50 per cent. was utilised by means of the muffle. At the commencement of calcination, it contained 26·44 per cent. of sulphur; on leaving the inclined portion of the muffle, where there was a low red heat, 8·20 per cent.; on leaving the horizontal portion of the muffle, where there was a bright red heat, 6·20 per cent.; at the end of the calcination 0·55 to 1·30 per cent. In 24 hours, 3½ tons of ore were roasted, with a consumption of 21 cwts. of coals. Five workmen on a shift worked the calciner. The gases escaping from the muffles into the sulphuric acid chambers carried from 5 to 6 per cent. by volume of sulphur dioxide. This furnace has, as compared with reverberatory furnaces, the drawback of heavier first cost and requires a heavier outlay for wages, but has, on the other hand, the advantage of utilising half of the sulphur dioxide evolved during calcination. But even allowing for the latter advantage, the costs of calcination in this furnace are heavier than the costs of calcination in long-bedded calciners. As compared with the muffle furnaces on the other hand, it has the objection that only a portion of sulphur dioxide evolved can be utilised. It has therefore been replaced by muffle furnaces.

A combined reverberatory and muffle furnace with horizontal muffles which gives very good results, is used at the Recke Works in Upper Silesia. It consists of a reverberatory furnace, over which there are two horizontal muffles connected together. The flame passes first over the hearth of the reverberatory furnace, surrounds first the lower and then the upper muffle. The products of combustion, together with the sulphur dioxide evolved from the reverberatory furnace, pass into towers in which they are freed from any sulphur dioxide and trioxide that they contain, and then into the stack. The sulphurous gases evolved in the lower muffle pass into the upper muffle, and thence together with the gases evolved in the latter, into the sulphuric acid factory. The blende is charged at the end of the upper muffle, passes, after it has traversed this, into the lower muffle, and finally into the reverberatory furnace. In this furnace 6 tons of blende are calcined down to less than 1 per cent. of sulphur in 24 hours, with a consumption of coal equal to 30 per cent. of the weight of the raw ore. This furnace, which is a modification of the Hasenclever furnace, gives better results than the original.

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[1] Mahler, *Annales des Mines*, vol. vii., book iii., p. 152, 1885.

Calcination in Muffle Furnaces

The necessity of neutralising the sulphurous gases evolved in calcining blende, and the difficulty of doing this when blende is calcined in reverberatory furnaces, have promoted the introduction within the last 20 years of muffle furnaces, in which the production of gases rich in sulphur dioxide, that is, containing 5 to 8 per cent. by volume and therefore suitable for sulphuric acid manufacture, can be combined with a complete calcination of blende. These furnaces depend upon the principles that the calcination must be conducted by means of heating the muffles externally by burning fuel, as also internally by the help of the heat developed by the oxidation of the sulphide of zinc; that the muffles should be arranged one below the other, and so combined that the blende which is to be roasted passes from above downwards, whilst the gases generated inside them, as well as those heating them from outside, move in the opposite direction. The first furnace designed on these principles, which admitted of the utilisation of the whole of the sulphur dioxide evolved in the calcination of blende for sulphuric acid manufacture, was designed by M. Liebig. He was followed by Grillo, Hasenclever, and a number of other inventors with furnaces depending upon the same principles, but of widely different design. These modern muffle furnaces have given such far better results than the older forms previously used, that they have replaced reverberatory furnaces as well as the combined reverberatory and muffle furnaces, wherever it is at all possible to find a market for sulphuric acid or to utilise sulphur dioxide in any other way. The furnaces that are at present in actual operation are built with fixed muffles. The ores are rabbled by means of hand power or mechanically. Muffles in the form of rotating cylinders have been proposed and patented, but have not yet come into regular use.

We must therefore distinguish:—

Calcination in Fixed Muffle Furnaces with hand rabbling.
Calcination in Fixed Muffle Furnaces with machine rabbling.
Calcination in Rotating Muffle Furnaces.

Calcination in Fixed Muffle Furnaces with Hand Rabbling

The most important furnaces of this class are those of Liebig and Eichhorn, and that of Hasenclever. A third furnace of the same type is that of Grillo.

The Liebig and Eichhorn furnace depends upon the principle of conveying the blende through a number of chambers lying one below the other, and of allowing the air required for oxidation to enter the chamber in a heated condition. The three upper chambers are heated by heat evolved by the oxidation of the sulphide of zinc similarly to the shelves of the Maletra furnace, whilst the lower chambers are heated externally by gas firing. The construction of the furnace, as patented,[1] is shown in Figs. 26 and

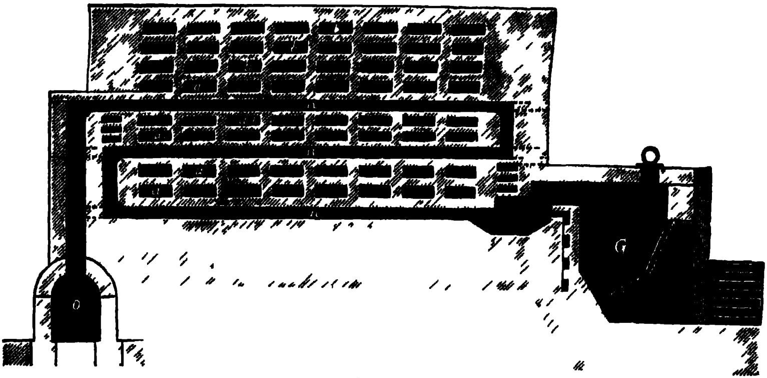

FIG 26

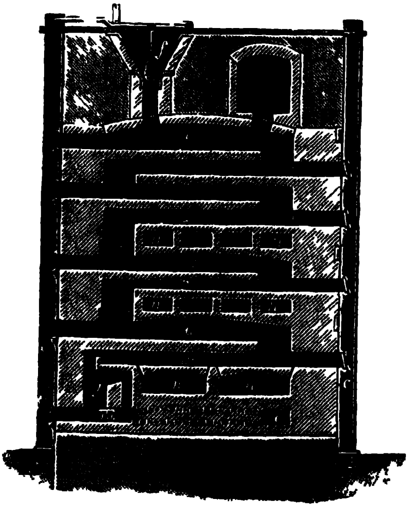

FIG 27

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[1] D R Patent, No 21,032

27. It consists of a shaft provided with muffles a^1, a^2, a^3, a^4, a^5, b', b'', b''', which are accessible by the working doors c disposed alternately along the two shorter sides. The heating of the chambers a^1, a^2, a^3 and a^4 is performed by means of the producer gas generated in the producer G, this being burnt in a stream of air heated by traversing flues in the walls of the producer. The flame traverses first the flues n, n, rises, passes through the flues n', n', traverses these flues, again ascends, and finally traverses the flues n'', n'', from which it escapes into the flue o leading to the stack. The air required for the oxidation of the sulphide of zinc enters by the opening d, passes into the flue e, and from the latter into the muffle a^1, being warmed on its passage through the walls of the flues n, n, and then traverses each separate muffle one after the other, oxidising the sulphide of zinc inside them. The zinc blende is delivered by means of a charging hopper f into the topmost muffle b''', and is transferred from the latter after some time into the muffle lying immediately beneath it. From this it is removed at definite intervals into the next lower lying muffle, and so it advances until it is drawn out from the bottommost muffle into the chamber g in a calcined condition. In the three topmost muffles the temperature is maintained entirely by the heat generated by the oxidation of the sulphide of zinc; in the lower chambers but little heat is derived from the blende, and they are therefore heated by means of producer gas from the outside. As this method of firing heats the lowest muffle to the highest temperature, the ore in its descent is exposed to gradually increasing temperatures, and finally reaches the end of the lowest muffle containing only 0·1 per cent. of sulphur. The sulphur gases traverse each muffle from below upwards and finally escape from the topmost muffle containing 6 to 8 per cent. by volume of sulphur dioxide. The ore remains in the muffle from 6 to 8 hours, and requires 48 hours to traverse the furnace. In experiments made to determine the degree of desulphurisation of the ore in the various muffles, it was found that it contained 27·8 per cent. of sulphur on charging into the topmost muffle; after being there 6 hours, 24·9 per cent.; in the four following muffles, 17·3, 13·2, 2·3 and 0·2 respectively, and when drawn from the bottom muffle only 0·1 per cent. According to Eichhorn[1] such furnaces yield in 24 hours from 4·2 to 4·5 tons of blende calcined down to 0·1 per cent. of sulphur, with a consumption of 0·8 ton of coal, 2 men being required on a 12-hour shift. Such furnaces are in use at Letmathe and at Hamborn, near Oberhausen. In Hamborn a block consists of 4 furnaces, and yields

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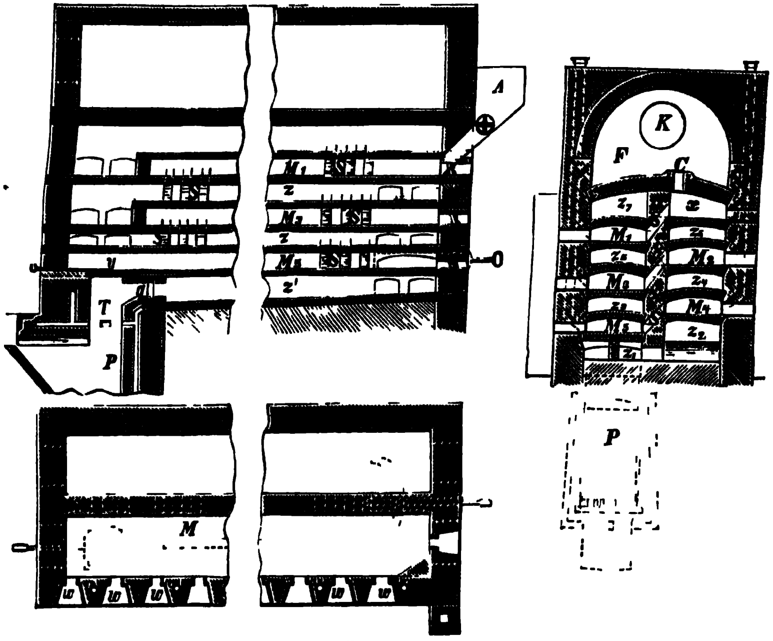
[1] Fischer's *Jahresber.*, 1889, p. 322.

in 24 hours 5 tons of calcined ore, with a consumption of 20 to 25 per cent. of coal, 2 men on a 12-hour shift working the furnace. The most recent furnaces of this type are those with 3 or 4 long-bedded muffles of which the lowermost is heated from below. In some furnaces there is also a flue between the bottommost muffle and the next higher one, so that the lowest muffle is heated from above and below, the next from below only.

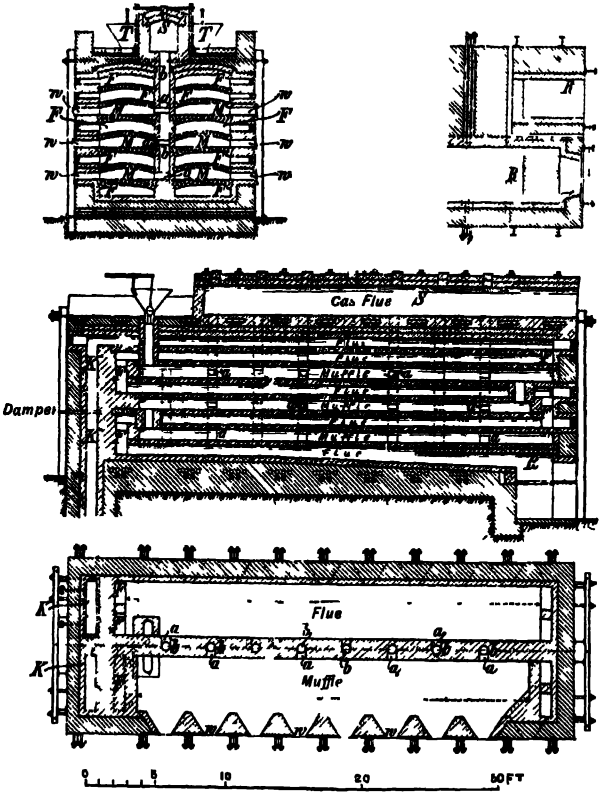
Grillo's furnace is shown in Figs. 28 to 30. It consists of the



Figs 28—30

muffles M^1 to M^5, and the flues Z^1 to Z^7. The ore is delivered by means of the hopper *A*, provided with a charging roller, into the topmost muffle which it is made to traverse, and at its end drops through the inclined slots *S*, into the next lower muffle. After passing through this, it is dropped into the muffle below and so gradually reaches the bottommost muffle, at the end of which it is drawn out through a working door. The products of calcination escape through the slots *S* out of the lower into the next higher muffle, and after they have travelled through all the muffles from below upwards, escape into the chamber *x*, from which they pass through the vertical flue *C* into the dust chamber *F*, and thence through the flue *K* into the sulphuric acid chambers. The furnace is fired by gas, but can also be fired by a grate. The gases generated in the producer *P* mix at *T* with air which has been warmed by traversing the furnace walls. The flame surrounding the muffles on three sides passes upwards through the flues Z^1 to Z^7, escaping from the topmost one into the stack; *w*, *w* are the working doors. Each individual muffle is 29 feet 6 inches long. By drawing out the slide *y* and closing the flue Z^1, by means of the damper *q*, the muffle furnace can be converted into a reverberatory furnace. This furnace has been found to be less efficient than that of Liebig, and has therefore been replaced at the Hamborn Works, where it was in use, by the Liebig furnace.

The Hasenclever furnace consists of several (three or four) muffles lying one above the other and united by means of vertical flues, and heated by the flames from a firegrate. The blende to be roasted is admitted by means of a charging hopper into the topmost muffle, and is pushed forward from time to time, as is done in long-bedded calciners; through a vertical flue at the end of this muffle it drops into the second muffle placed below the former, in which it is pushed forward in the same way, drops thence into the third muffle, and so on. At the end of the bottommost muffle the calcined ore is drawn out from a working door. The flame follows the opposite direction to the calcined ore, passing upwards, and on its way heats the floors and arches of the various muffles. The products of calcination either pass from below upwards through all the muffles, or else escape from the rear of each muffle by vertical flues, from which the gas escapes to a main flue leading to the sulphuric acid works. With ores rich in sulphur, two or three muffles have also frequently been placed one above the other, and the flame has been allowed to heat the floor of the lower and the roof of the upper muffle; in order to economise heat, these furnaces are always built in pairs back to back. The construction of the Hasenclever furnace is shown in Figs. 31 to 34, which represent a pair of such furnaces. *R*, *R* are the grates, *M*, *M* are the individual muffles, *F*, *F* are the flues by which the flame passes from below upwards, and from the topmost of which it then escapes from the flue *K* into the stack. *T*, *T* are the charging hoppers from which the blende to be roasted is conveyed to the topmost muffle and then traverses one muffle after the other; *w*, *w* are working doors through which the blende is rabbled and pushed forward. In this particular case the products of calcination are drawn off separately from each muffle. They escape through openings *a* in the rear wall of the furnace into vertical flues *b*, and thence through the main flue *S* to the sulphuric acid works. As above noted, this method of collecting the products of calcination has been discontinued, and they are now made to traverse the whole of the muffles, and escape from the uppermost one to the main flue. Such



Figs 31—34

a furnace calcines in 24 hours about 4 tons of blende down to 0·6 to 1·06 per cent. of sulphur, consuming a quantity of good coal equal to 20 to 25 per cent. of the weight of the raw ore. Two men on a shift are sufficient to work the furnace. Recently this furnace has been improved by cutting each muffle into two by means of vertical walls across the centre, and so uniting the halves lying below each other by vertical flues that the blende has only to traverse these halves of the muffles that lie one above the other, in a downward direction, the calcination being in nowise injured thereby, although the blende only has to travel half as far as it had to in the older form. At the same time, with ores rich in sulphur, the two lowermost muffles alone are heated externally, the upper ones receiving only the heat generated by the oxidation of the sulphides. By these means the output of the furnace has been increased by 30 per cent., and the labour required has been diminished by 25 to 30 per cent. The flame takes the same course as previously. Furnaces of this construction are at work, for example, at the Guido Works, near Chropaczow, at the Silesia Works near Lipine, at the Recke Works near Rosdzin, at the Munsterbusch Works, and at the Rhenania Works, both near Stolberg

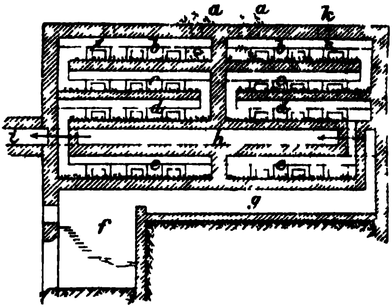


FIG. 35

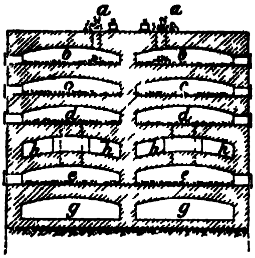


FIG. 36

The most recent furnaces have muffles 40 feet 9 inches long and 5 feet broad. Each muffle is divided by a partition into two divisions, each of which is 20 feet 4 inches long. The arch of the muffle is 9 inches high at the centre, and 5 inches at the sides. Each muffle has ten working doors, that is to say five for each half, which can be closed by cast-iron slides. The air employed for oxidation is heated in flues which lie beneath the lowest draught-flue. The construction of the furnace at the Guido Works[1] is shown in Figs. 35 and 36, in which *f* is a step-grate, the flame from which heats the two muffle divisions *e*, and the floor of the muffle divisions *d*, traversing the flues *g* and *h* into the flue *i* leading to the stack. The ores are dried upon the roof of the furnace, and are then charged through the openings *a*, *a* into the topmost muffle divisions *b*, *b*. Thence they pass into the divisions corresponding to each half of the furnace, *c*, *d* and *e*, and after the calcination is complete are drawn out from the divisions *e*. The gases produced in calcination traverse the various muffles, and escape through the openings *k* from the topmost muffle into a main flue. There are two men on the shift, or four in 24 hours, during which time 5 tons of zinc blende are roasted with a consumption of coal equal to 20 per cent. of the weight of the raw ore.

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[1] *Berg. und Hutten Ztg.*, 1891, p. 430.

At the Silesia Works, near Lipine, in the year 1895, a furnace of similar construction was calcining 5 tons of blende down to 1 per cent. of sulphur in 24 hours, with a consumption equal to 25 per cent. of inferior coal. The number of workmen in 24 hours was four, *for calcining and firing, and ⅛ for charging* the blende and delivering coal. The gases evolved during calcination contained 5 per cent. by volume of sulphur dioxide.

At the Recke Works, near Rosdzin in Upper Silesia, in 1895, a furnace with 3 muffles, of which the lowest is heated by the flames from below, and the uppermost from above, calcines 3·5 tons of zinc blende in 24 hours down to 1·5 per cent. of sulphur, 1·2 tons of coal being used. There are 2 men on a 12-hour shift. The gases evolved contain 6 per cent. by volume of sulphur dioxide.

At the Stolberg Works ores containing 27 to 28 per cent. of sulphur are roasted down to 0·5 to 1 per cent., when they are free from lime or magnesia; otherwise they retain 2 to 3 per cent. of sulphur. In 24 hours 8 tons of ore are calcined in a block consisting of a pair of furnaces, with a consumption of coal equal to 20 per cent. of the calcined ore. A crew of 4 men works the furnace block on each shift. The desulphurisation of blende and the formation of sulphate of zinc during calcination in the Hasenclever furnace of most recent construction is shown in the following table of analyses, which were executed at the Rhenania Works. A is uncalcined ore, Z is calcined ore, 2 to 14 are the various samples taken during the process of calcination:—

Sample	Zinc Sulphide per cent	Zinc Sulphate per cent.	Zinc Oxide per cent
A . . .	57·2	0	0
2 . .	53·5	3·5	0·8
3 . . .	53·0	3·8	3·4
4	48·4	4·2	4·6
5 . .	39·9	4·3	12·3
6 . . .	35·2	5·0	16·5
7 . . .	34·8	6·9	17·0
8 . .	25·2	6·3	27·1
9 . .	24·2	5·2	30·0
10 . . .	19·2	5·8	32·6
11	10·0	7·8	40·0
12 . . .	7·9	6·2	44·9
13	1·5	4·7	52·5
14	1·6	2·6	53·0
Z	1·2	0	55·0

The Hasenclever furnace has fairly established itself in the Rhine provinces and Silesia, and has there replaced the older Hasenclever-Helbig furnaces completely, and reverberatory furnaces in great part.

Calcination in Fixed Muffle Furnaces with Machine Rabbling

Such furnaces are employed with advantage in districts where the rate of wages is very high. They consist of muffle furnaces with some mechanical rabbling appliance which receives either a rotating or a reciprocating motion.

The Haas[1] furnace is a furnace with rotating rabbles. It is distinguished from the McDougall furnace described in Volume I., p. 66, by the chief difference that the separate circular muffles are not separated from each other by solid arches, but by hollow flues, through which the products of combustion can circulate. By means of the revolving rabbles the ore is successively drawn through four chambers, lying one beneath the other, and then reaches, if necessary, the floor of a rectangular muffle, which is the first to be heated by the flames, and in which the last portions of sulphur are removed from the blende. The construction of this furnace[2] is shown in Figs. 37 to 39, in which *a*, *a* are the four muffles, through the midst of which the shaft *x*, provided with rabble arms, passes. Each pair of muffles lying one above the other is connected by means of the flues *b* for the products of combustion, and the vertical shafts *n* for the passage of the ore; *c* are flues communicating with the stack, and which consist of chambers between the individual muffles and of vertical flues which connect these chambers. The gases are generated in a producer, and pass through the flue *d* into the heating flues; they pass in the direction indicated by the arrows, and after they have heated the topmost muffle, escape through a descending vertical flue into the horizontal flue *e*, which leads them into a regenerator for heating the air used for oxidation. The latter enters the bottom muffle at *f*, and traverses, together with the gases evolved, the whole of the muffles. These gases escape from the topmost muffle through the flue *p* to the works where they are to be utilised. The blende is charged into the topmost muffle through the shaft *m*, rabbled by the tines of the rabble arms, and gradually moved forwards towards the lower muffles. The shaft *x* can be turned to the left as well as to the right, and has two cast-iron arms in each muffle. The individual tines *h*, fastened to one arm, are movable, whereas those carried by the other arm are fixed and are set obliquely. By means of the lever *k*, the tines, *h*, can be so placed that the pulverulent blende may be pushed either towards the centre or towards the circumference. When the ore from the upper muffle is to be transferred to the one next below it, the tines *h* are so placed that they push the ore towards the circumference. It then drops through the slot *n*, which can be closed by a slide when desired, into the muffle below, and thence subsequently in the same way into the next lower muffle, and finally into the last muffle. From the last muffle it is discharged similarly through the slot *o*. The discharged ore either drops into a vault or into a long rectangular muffle not shown in the figure, in which it is roasted dead. The products of calcination escape from this rectangular muffle into the bottom round muffle, and pass in the same direction as the gases developed in the latter. The flame

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[1] D. R. Patent, No. 23,081.

[2] *Berg. und Hütten. Ztg.*, 1884, Plate I., Figures 12-34.

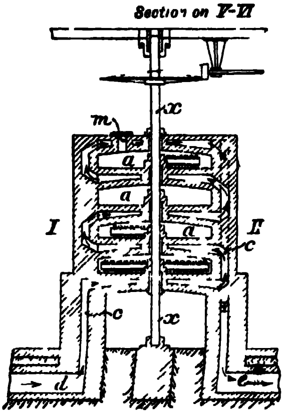
Section on V-VI

Fig 37

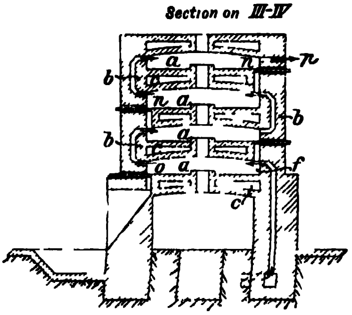
Section on III-IV

Fig 38

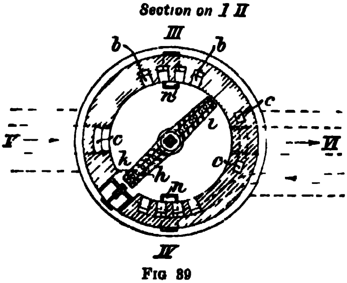
Section on I II

Fig 39

first heats the rectangular muffle by means of various flues, and then passes into the flue c for the round muffles. The gases produced in this furnace contain from 6 to 7 per cent. by volume of sulphur dioxide. Such furnaces are in operation at Oberhausen for the calcination of blende containing on the average 25 per cent. of zinc.[1] The size of the grains should not be less than 0·08 inch. The hearths are 8 feet 2 inches in diameter, and the thickness of each floor amounts to 4 inches. From the bottom circular muffle the ore passes on to two hearths, lying one above the other, each 19 feet 8 inches in length, with 4 working doors in each, upon which it is roasted dead by means of hand labour. The gases from the muffles are employed for the manufacture of sulphuric acid. One workman is required for each furnace, the output of which is equal to 3·4 tons of blende per 24 hours. The consumption of coal for calcination amounts to 17 per cent of the weight of the calcined ore, and for the production of power to 5 per cent. The calcined ore contains on the average 1 per cent. of sulphur.

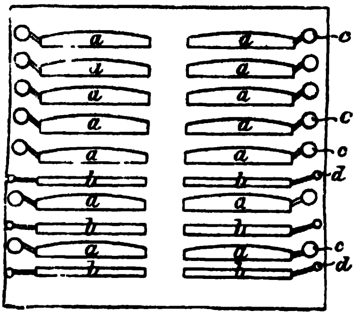

FIG. 40.

At the works of Hegeler and Matthiesen, at La Salle, in Illinois, U.S.A., multiple muffle calcining furnaces with mechanical rabbles are in use. Such a furnace has 7 muffles one above the other, each of which is 46 feet long and 4 feet 6 inches broad. The three lowermost muffles are heated by means of producer gas, the flame passing first below and then above them. Two furnaces are united to form one block. There is one rabble common to the two muffles which lie side by side. It is moved at intervals of an hour by means of a rod moved by friction wheels backwards and forwards through the blende spread out in the muffles. Such a double furnace calcines in 24 hours 23 tons of zinc blende, with a consumption of 4·8 tons of refuse coals.[2] In Fig. 40, a are the muffles, and b the flues; c are flues through which air is conveyed to the muffles, and d the flues for introducing air into the fire-box.

The Rhenania Chemical Works at Stolberg has patented a Hasenclever furnace with mechanical rabbles.[3] This furnace consists of four muffles lying one immediately above the other, through which an endless chain provided with rabbles and scrapers at fixed distances apart, is kept moving. The rabbles stir the ore, whilst the scrapers move it forwards. The ore is charged into the topmost muffle, and then gradually transferred to the lower ones, until it is discharged from the bottom muffle in the calcined state. In order not to expose the endless chain to the flames there are no flues between the separate muffles. The flames, therefore, are carried round the muffles in one single flue. The description of the furnace as given in the Patent, 1892, page 321, resembles that of the O'Harra furnace, as described in Vol. I., page 72. Nothing is yet known respecting the practical use of this furnace.

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[1] *Rev. Universe des Mines*, 1894, p. 38. [2] *The Mining Industry*, 1894, p. 215.

[3] D. R. Patent, No. 61,043.

Calcination in Furnaces with Movable Working Chambers

Such furnaces are formed by rotating cylinders in which the flame is kept separate from the ore. Such a furnace has been proposed by Koehler in Lipine.[1] It consists of a rotating cylinder of cast- or wrought-iron, lined with firebrick, and fired with gas. In that portion of the lining which is nearest the interior of the furnace there are flues parallel to the axis of the cylinder traversed by the burning gases. In that portion of the lining nearest the outside of the furnace there are air flues running parallel to the heating flues. In the former, the air required for oxidation, which moves in the opposite direction to the products o combustion, is first heated and enters at one end of the cylinder through a tube lying in the axis of the furnace. The products of calcination escape at the opposite end of the furnace by means of another tube also lying axially. The zinc blende is automatically charged into the furnace by means of an apparatus attached to a hopper, and is automatically discharged at the opposite hottest end. The furnace is thus continuous acting. In the interior of the furnace there are walls provided with apertures which separate the furnace to some extent into different chambers, the object of which is to prevent the products of calcination, concentrated in the last chambers, from striking back. This furnace has been tried on an experimental scale at Lipine, and is said to have given very satisfactory results. Up to the present, however, it has not been definitely introduced, on the ground of the not inconsiderable first cost thereof. A rotating cylinder with the flues in the centre of the furnace—the Douglas furnace—has also been proposed for the calcination of sulphides. It is described and figured in Vol. I., page 85.

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[1] D. R. Patent, 57,522, May 7, 1890.

UTILISATION OF THE PRODUCTS OF CALCINATION

The products of muffle calcination have up to the present, with but few exceptions, been used exclusively for the production of English sulphuric acid, the method of manufacture of which may be taken as known. They may also, however, be used for the preparation of sulphuric anhydride, of fluid sulphur dioxide, of sodic sulphate, of sulphuretted hydrogen, of sodium hyposulphite, of sulphur, and for the solution of copper. The preparation of these bodies, with the exception of the sulphur, can only be carried out with advantage under certain local conditions, on account of the small demand.

Sulphuric anhydride is manufactured at the Mulden Works near Freiberg, and at the Rhenania Chemical Works near Stolberg, from the products of calcination of pyritic lead and silver ores, or from pyrites which are burned in kilns and Hasenclever furnaces, or in pyrites burners. The products of calcination of zinc blende in muffle furnaces could be equally well employed for this purpose. On account of the limited market for sulphuric anhydride, which is employed for the production of Nordhausen sulphuric acid, which again is used in the ozokerite and aniline manufacture, no attempts have been made in this direction at any of the blende calcining establishments. In the manufacture of sulphuric anhydride, the products of calcination are first led into lead chambers filled with fragments of coke, of burnt clay or of quartz, over which concentrated sulphuric acid trickles, and then pass through vessels heated externally, inside which platinised asbestos is contained. The object of the first portion of the process is the removal of water vapour, whilst by the means of the catalytic action of the platinum, sulphur dioxide and oxygen are united to form sulphur trioxide. As the gases produced in calcination are greatly diluted by means of nitrogen and air, only half of the sulphur dioxide at the outside is converted into sulphuric anhydride. From the last-named vessels the gases carrying sulphuric anhydride are led into towers in which concentrated sulphuric acid is trickling down, so as to absorb the anhydride, which is distilled off from the solution of anhydride in sulphuric acid thus produced. The gases escaping from the absorption towers still contain the sulphur dioxide which has not been converted into sulphuric anhydride, and these are then conducted into lead chambers for sulphuric acid manufacture.

The fluid sulphur dioxide is manufactured from the products of calcination of zinc blende in muffles, at the zinc works of Hamborn near Oberhausen, and the Silesia Works near Lipine. Having regard to the still restricted applications of fluid sulphur dioxide (for the manufacture of sulphite cellulose, for the production of cold, for the manufacture of sugar, and for bleaching), and to the great expenses entailed by the plant for its manufacture, it is not to be expected that its production from the products of calcination will take any extension in the immediate future. At the Guido Works, near Chropaczow, in Upper Silesia, where the process has been in use for some considerable time, it has lately been stopped, sulphuric acid works being in process of erection there. The process employed was invented by Schröder and Hänisch. As it separates gaseous sulphur dioxide from the gases evolved from the muffle furnaces in a condition of great concentration, in which it may also be employed for other purposes, it deserves somewhat fuller consideration. The process[1] consists in absorbing sulphur dioxide out of the gases by means of water trickling through a coke tower, in expelling from this water the sulphur dioxide in a concentrated state mixed only with a small amount of water vapour by means of heat, in separating the moisture from the mixed gases by means of concentrated sulphuric acid or calcium chloride, and in condensing the concentrated gaseous sulphur dioxide thus obtained by means of a compressor. This process does not admit of the preparation of concentrated sulphur dioxide from the gases of reverberatory furnaces with advantage; it can only be produced from gases which contain at least 4 per cent. by volume of sulphur dioxide, such as are evolved from shaft furnaces and muffle furnaces. As regards the execution of the process, the absorption of the sulphur dioxide is performed in coke towers through which water trickles. The sulphur dioxide is expelled from the water in three forms of apparatus, in which the heat of the products of calcination in part, and in part the latent heat of water vapour which is developed when the sulphur dioxide is expelled from the water containing the latter, in part the residual heat of the water freed from sulphur dioxide, are all utilised. The acid water is first conveyed into a system of low lead chambers in which it is warmed by means of the water from which the acid has been driven off, which surrounds these chambers. Thence it passes into closed leaden tanks under which pass the hot gases as they escape from the furnace before they pass into the absorption tower. The heat which they give off to the tanks raises the fluid contained in the latter to the boiling point. The sulphur dioxide escapes, in consequence, from the boiling solution and enters the dehydrating apparatus. The boiling fluid, not however quite free from acid, is drawn off from the leaden tanks into a so-called *colonne*, in which the last portions of sulphur dioxide are removed from it by the direct action of steam, the steam being separated from the sulphur dioxide by means of a spray of cold water. The hot water, now free from acid, is used for heating the acid water as it first escapes from the absorption towers, by allowing it to escape from the *colonne* through a system of lead chambers which surround the lead chambers containing the acid water. Water vapour is best separated from the sulphur dioxide which has been driven out of the water, by allowing the gaseous mixture to ascend through a tower filled with coke, down which concentrated acid is trickling, which absorbs all the water. The sulphur dioxide, thus completely dehydrated, is compressed into the fluid state by means of a pump made of bronze, and is collected in iron vessels of sufficient strength.

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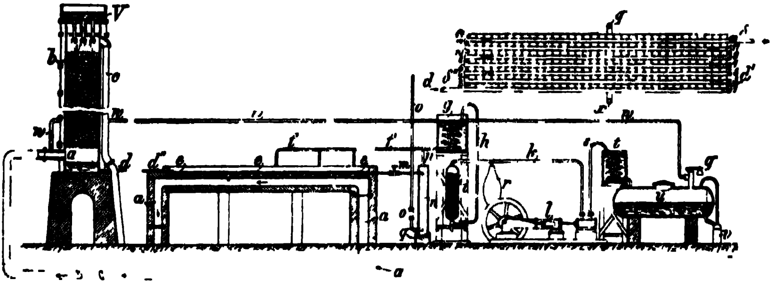
[1] D. R. Patents, Nos. 26,181, 27,581, and 36,721.



Figs 41 and 42

The pressure that has to be employed varies according to the season from 2 to 3½ atmospheres. The intermixed, difficultly compressible gases are allowed to escape into the absorption tower by means of a valve placed in the receiver. The fluid sulphur dioxide is shipped in iron vessels. It contains 99·8 per cent. of pure SO_2. The gases evolved from the calcination of zinc blende at Hamborn and Lipine contain about 6 per cent. by volume of sulphur dioxide; in the absorption tower this is removed from the gases down to 0·05 per cent. by volume. The water which flows out from the towers contains 12 pounds of sulphur dioxide in 100 gallons.

The construction of the plant for the production of fluid sulphur dioxide from the products of calcination is shown in Fig. 41.[1]

The gases pass from the calcination furnace through the flue *a* into the absorption tower *b*. On their road to the latter they give off their heat to the leaden tanks *e*. They ascend in the lead tower filled with coke and are freed from their sulphur dioxide by means of water coming from the distributor *V*. The gases that reach the top end of the tower, consisting of nitrogen, oxygen, and very minute quantities of sulphur dioxide, are conveyed by the descending tube *c* into the stack. The water containing sulphur dioxide in solution escapes from the pipe *d* at the foot of the tower first into a heating apparatus, which is omitted in Fig. 41, but is shown separately in Fig. 42. It consists of a series of flat leaden chambers each 16 inches deep, disposed one above the other, these lead chambers forming two systems. In the one system the fluid solution which is to be warmed ascends, whilst in the other system the hot water descends, giving off its heat to the ascending fluid. For this purpose the chambers are so arranged that a chamber of the one system alternates regularly with one of the other. In the chambers marked with odd numbers, 1, 3, 5, 7, 9, 11 and 13, the acid solution is ascending, whilst in the chambers with even numbers, 14, 12, 10, 8, 6, 4 and 2, the hot water is flowing down. The adjacent chambers of each system are so united with each other that the combination takes up the whole side of the chamber. The individual chambers are stayed by means of strips of lead made fast inside them, these lying in the direction of the flow of the solution. The acid water escaping from the absorption tower enters at *d* into chamber No. 1, rises at d' into chamber No. 2, at d'' into No. 3, and so on, till it escapes at δ' from the last chamber 13 in a heated state, entering the leaden tanks *e* at d''. The hot water passes in the opposite direction. It enters the topmost chamber 14, through the tube *g*, flows through it and passes from the end of it by a tube not shown in the figure into the chamber 12; from this into No. 10, and so on until it escapes at the end of chamber No. 2 through the tube *x* after having given off the greater portion of its heat. The acid solution which has thus been warmed passes through the tube d'' into the leaden tanks *e*, which it traverses one after the other. It is here heated to boiling point by means of the hot products of calcination passing underneath the tanks, and in consequence gives off sulphur dioxide mixed with a certain amount of water vapour. This gaseous mixture flows through the tube *f* into the water cooled worm *g*, in which a portion of the water vapour is condensed; thence it flows back through the above-named pipe into the tanks or into the *colonne*, and thence through the tubes *h* into the drying tubes *i*, in which the last portion of the water vapour is retained by means of coke soaked in concentrated sulphuric acid. From the drying chamber the sulphur dioxide passes through the tube *k* into the compressor. In order to regulate the pressure a silk bag *r* is interposed in the tube *k*. According to the size of this bag the movement of the pump *l* is regulated. The gas is forced through the tube *s* into the worm *t* in which it is liquefied. The liquid sulphur dioxide flows out of the worm into a wrought iron tank *u*. The gases, oxygen and nitrogen, which are carried with the fluid, escape when the valve *g* at the top of the tank is opened, into the tube *w*, which leads them to the absorption tower. The fluid sulphur dioxide is drawn off from the tank into wrought iron cylinders *v* holding 110 or 120 pounds, or else into tank wagons holding 10 tons.

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[1] *Zeitschr. f. Angewandte Chemie.*, 1888, p 448; Lunge, *Soda Industrie*, vol. i., p 264.

The boiling solution that remains behind in the tank *c* contains a small quantity of SO_2; to extract the latter it is run through the tube *m* into the *colonne* *n*, where it is raised to boiling by means of vapour entering from below through a tube *o*, whilst water is sprayed into the upper end. The sulphur dioxide and the steam rise in the tower, are in part condensed by the water trickling down and expelled again when the latter reaches the bottom. Of the gas escaping from the upper end of the *colonne*, the steam is condensed by the water spray and flows down with the latter. A portion of the sulphur dioxide is here absorbed by means of this water. As the quantity of the latter only suffices for the absorption of a relatively small proportion of the sulphur dioxide, the greater portion of the gas escapes from the tube *p* into the worm *g*, and there unites with the gas evolved from the tanks *e*. The solution trickling down in the *colonne* gradually loses its sulphur dioxide as it is raised to the boiling point by the steam, and thus reaches the bottom of the *colonne* free from sulphur dioxide; thence it escapes through the tube *q* into the above-described lead chambers and warms the acid water coming from the absorption towers. The *colonne*, which consists of a tower, the lower portion of which is filled with circular tiles and the upper portion with coke, has recently received certain improvements.[1] It is shown in Fig. 43 (D. R. P. 36,721). The hot steam enters at *a*; a water spray is produced by the rose *b*; through the tube *d* sulphur dioxide escapes; through the tube *e* the solution escapes after it has been freed from acid and has been heated to the boiling point. By means of the circular tiles, the solution that is trickling down is delayed, and thus better exposed to the action of the ascending steam. The cylinders in which fluid sulphur dioxide is sent into the market are shown in Figs. 44 and 45. They have a screw valve *c* which is protected by the cap *a* when they are being transported. If sulphur dioxide is to be employed in the gaseous form the bottle is placed vertically (Fig. 44) The spindle of the screw valve *c* is turned by means of a key and opens the pipe *b*; through the latter gaseous sulphurous acid then escapes and continues to escape until the temperature in consequence of the evaporation of the solution falls to − 10° C. A further quantity of gas can then only escape when the cylinder has taken up from its surroundings the requisite quantity of heat. If the sulphur dioxide is to be utilised in the fluid state the cylinder is laid down so that the small tube *b* is uppermost. By means of the pressure of the gas, fluid sulphur dioxide is then forced out through this tube. The whole contents of the bottle can be expelled by means of the bent tube *n* which reaches to the bottom. In order to avoid explosions the cylinders are tested to a pressure of 50 atmospheres. The vapour tension of sulphur dioxide amounts at 10° C. to 1·6 atmospheres; at 20° to 2·4; at 30° to 3·51, and at 40° to 5·15 atmospheres. These bottles are best preserved in some locality where the temperature does not exceed 40°.

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[1] D. R. Patents, Nos. 36,721, 52,025.

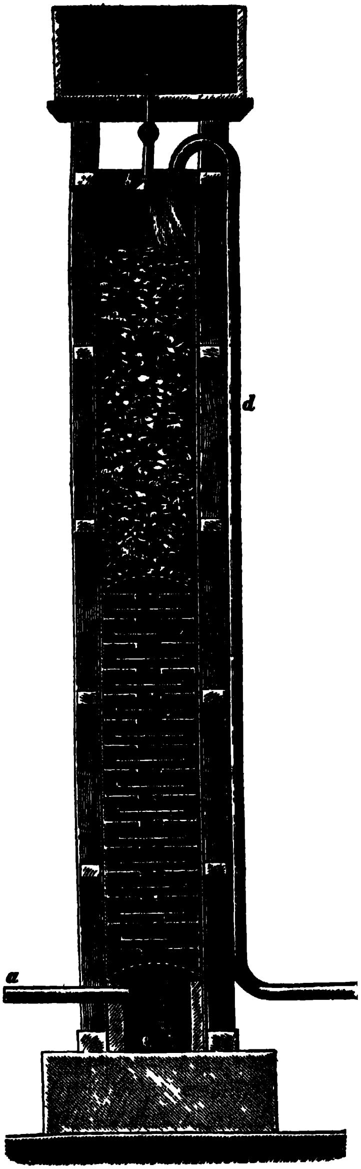

FIG 43.

Sulphur dioxide evolved from muffle furnaces is also suitable for the preparation of sodium sulphate from common salt, according to the process of Hargreaves, which has been practised in a number of English soda works, and since the year 1890 at the Rhenania Works. It consists in leading the products of calcination mixed with air and water vapour into a cast-iron cylinder heated externally, inside which spherical pieces of salt are arranged upon an iron grating. Sodium sulphate is thus formed with the evolution of hydrochloric acid.

These sulphurous gases are also available for the production of sulphuretted hydrogen by passing them, mixed with water vapour, through shaft furnaces filled with glowing coke, which is kept at a red heat by passing air from time to time over it. Sulphuretted hydrogen forms in accordance with the equation:—

$$SO_2+H_2O+3C=H_2S+3CO$$

Sulphuretted hydrogen is, however, used but rarely, and only in limited quantities, for the precipitation of metals such as copper and silver from their solutions, so that there is no probability that this process will be introduced into blende calcining establishments.

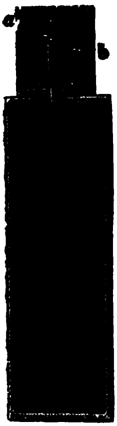

FIG. 44.

FIG 45

Sodium hyposulphite can be produced from these gases, by passing them through a solution of sodium sulphate, the salt being formed and sulphur produced simultaneously. Its employment for the extraction of silver is, however, a very limited one, so that the utilisation of the products of the calcination of blende for this purpose does not seem practicable.

Although there is a large demand for sulphur, its production from the gases evolved from muffle furnaces is tolerably expensive, and has not, therefore, been conducted on a large scale. It can be produced from these gases directly by passing them into solutions of the polysulphides of sodium or of calcium, and by allowing the gases to act upon sulphuretted hydrogen, or indirectly by first separating out the sulphur dioxide and reducing the latter by carbon or coal gas. Polysulphides of the alkaline earths will only be used for the manufacture of sulphur when they can be obtained free of cost as the various bye-products of other processes, such as the decomposed residues from Le Blanc soda works. By means of sulphuretted hydrogen, sulphur can be obtained from the products of calcination by allowing both gases to ascend through wooden towers in which a solution of calcium chloride is trickling down, sulphur being formed in accordance with the equation:—

$$2H_2S + SO_2 = 3S + 2H_2O.$$

The gases are introduced at the bottom of the tower, whilst the solution of calcium chloride which causes the sulphur to separate out, enters at the top and trickles down the tower, flowing over wooden plates inclined alternately in opposite directions. The sulphur, which is thrown down upon these boards, escapes with the solution of calcium chloride from the towers into a series of vats placed one below the other, in which it is deposited, whilst the clear solution is pumped up to the top of the towers to be used over again. The sulphur is melted according to Schaffner's method under water by means of steam at 2½ atmospheres pressure Sulphuretted hydrogen can be produced (unless it is available as a bye product of certain processes) as described above, viz., by leading a portion of the products of calcination, together with water vapour, through a column of red-hot coke. It may also be produced according to Chance's method, by treating residues from the Le Blanc soda works by carbon dioxide. This process can only be recommended when sulphuretted hydrogen is available without any great expense.

Sulphur can only be produced by the reduction of sulphur dioxide by carbon when the gases are in a concentrated form, such as are employed for the manufacture of the fluid sulphur dioxide according to the Schroder and Hanisch process. It cannot therefore be produced direct from the gases from muffle furnaces, but only after a previous concentration of the latter by the aid of water In the earlier experiments for the production of sulphur from the diluted gases a portion of the carbon was burnt to waste in consequence of the air contained in the gases; moreover, in consequence of the dilution of the sulphur dioxide by indifferent gases, its reduction to sulphur was only very imperfect. The extraction of sulphur from the sulphur dioxide concentrated as above described has been patented by Schroder and Hanisch. The concentrated sulphur dioxide is first passed through a muffle filled with red-hot coke, and then through a second vertical muffle which contains red-hot indifferent bodies known as "intact bodies," such as firebricks, burnt clay, &c. In the muffle filled with coke about half of the sulphur dioxide is reduced to sulphur, while in the second muffle the sulphur dioxide which still remains and the gases formed in the first muffle, viz., carbon monoxide, carbon bi-sulphide, and carbon oxy-sulphide, act upon each other, the products being carbon dioxide and sulphur. The sulphur vapours and carbon dioxide escape from the second muffle into a condensing chamber in which the greater portion of the sulphur is deposited in the fluid state, and a small portion as flowers of sulphur. In some experiments tried at the Grillo Zinc Works 99 per cent. by volume of sulphur dioxide was thus reduced to sulphur. The gases escaping from the condensing chamber contain 96 to 97 per cent by volume of carbon dioxide, and 2 to 3 per cent of carbon monoxide. According to the patents of Schroder and Hanisch, the reduction of sulphur dioxide can also be performed by means of carbon monoxide, coal-gas, or any other gas rich in carbon. As to the economic results obtained by the extraction of sulphur in the above manner no opinion can be given at the present time, as it has not been carried out on a large scale. The concentrated sulphur dioxide produced by means of water has hitherto been used exclusively for the production of fluid sulphur dioxide.

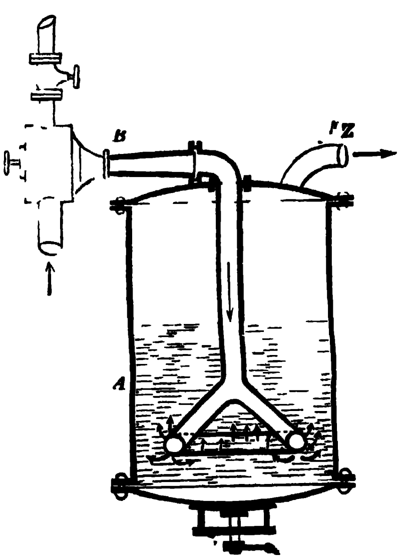

Fig. 46

The utilisation of the gases from muffle furnaces for the dissolving of copper is only possible under local conditions, and even then on a very small scale, as, for example, the extraction of copper from poor oxidised or acid copper ores, or for dissolving copper from cement copper containing gold or silver. In the first-named case the gases produced in calcination, together with water vapour and nitrous gases, are allowed to act upon the ores lying upon a grating composed of stone or wood. In the second case Rossler's arrangement may be used. The latter is shown in Fig. 46, and consists of a vessel of wrought iron *A*, containing a solution of sulphate of copper. By means of a Körting injector *B*, the gases are forced in fine jets through a ring into the solution. The sulphur dioxide is thereby converted into sulphuric acid, the sulphate of copper being at the same time reduced to cuprous sulphate. The sulphuric acid thus formed dissolves the cement copper containing gold and silver, the latter metals being left behind. Nitrogen and oxygen escape through the tube *Z*. This arrangement is employed at the parting works in Frankfort-on-the-Main, where the gases which contain the sulphur dioxide are produced by the solution of auriferous silver in boiling concentrated sulphuric acid.

2. THE PROCESS OF REDUCTION, OR THE EXTRACTION OF ZINC FROM THE CALCINED ORES

The reduction of zinc from the calcined ores is performed by heating the latter with carbon to a white heat in fireclay vessels. Zinc is then separated in the form of vapour and is collected in clay vessels known as receivers or adapters. The process of reduction is therefore a process of "compound volatilisation" or of distillation. The ores which are to be subjected to this process contain zinc in the form of oxide or silicate. In consequence of the imperfect calcination of zinc blende, small quantities of zinc may be present as sulphide or sulphate. In the presence of iron any sulphur is combined with this metal. Of foreign bodies, the calcined zinc ores contain oxides and silicates of iron and manganese, sulphide of iron, lead oxide, sulphate and silicate, silicates of alumina, quartz, calcium and barium sulphates, antimoniates and arseniates, lime, magnesia, cadmium oxide and silver. Zinc is reduced from its oxide both by carbon and carbon monoxide. By its reduction by carbon, carbon monoxide is formed, which again reduces more zinc, with the formation of carbon dioxide. In what proportion the carbon monoxide contributes to the reaction is not known. In any case the carbon dioxide produced is immediately reduced to carbon monoxide by the excess of carbon present, so that it has no opportunity of re-oxidising the zinc vapours. It is only when carbon is deficient that the carbon dioxide could re-oxidise the zinc at a red heat. The fact that the gas escaping from the reducing apparatus after the commencement of distillation really only contains very small quantities of carbon dioxide is proved by the following analyses[1]:—

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[1] *Dingl. Polyt. Journ.*, 237, 390 (Fischer); *Berg. und Hutten. Ztg.* 1880, 371.

GASES FROM RETORTS, LETMATHE.

	1	2	3	4	5
Carbon dioxide	0·48	1·06	0·11	1·10	0·82
Carbon monoxide	not det.	92·16	97·12	not det.	98·04
Hydrogen	5·32	1·83	not det.	,,	0·72
Nitrogen	not det.	1·01	0·41	,,	trace

The gases of column 5 escaped immediately before the end of the distillation. Before the commencement of distillation the gases contained a considerable quantity of carbon dioxide and hydrogen, as also a certain amount of methane, as is shown by the following analysis[1] :—

Carbon dioxide	15·58
Carbon monoxide	38·52
Methane	4·17
Hydrogen	41·70
Nitrogen	trace

The methane and a portion of the hydrogen are produced by the gases evolved from the lean coal, which is used as reducing agent. Another portion of the hydrogen is derived from the decomposition of the water vapour, contained in the charge, by the red-hot coal. This decomposition also produces a portion of the carbon dioxide and monoxide. Another portion of the oxides of carbon is produced by the action of the air still present in the vessel upon the carbon. The gases which escape from the muffles in the process of reduction at the Munsterbusch Works, near Stolberg, show the following composition :—

	1	2
Carbon dioxide	0·09	0·11
Carbon monoxide	95·36	97·42
Hydrogen	3·72	1.20
Nitrogen	0·61	0·92

Zinc can only be reduced from its silicate by solid carbon with the formation of carbon monoxide.

The zinc vapours escape, together with the gases formed during reduction, from the vessels into an adapter in which they are condensed, whilst the gases escape either direct into the air or into arrangements in which metallic particles carried off by them may be deposited. Any zinc present in the form of sulphide is not attacked by carbon, and therefore remains in the residues of the distillation. Only in case the ores contain considerable quantities of iron oxide or basic silicate of iron is iron reduced from these substances by the carbon, the iron reducing any sulphide of zinc to metallic zinc. The formation of sulphide of iron is not, however, desirable, because it destroys the vessels used for distillation.

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[1] *Dingl. Polyt. Journ.*, 237, 390 (Fischer) ; *Berg. und Hütten. Ztg.* 1880, 371.

Any *sulphate of zinc* present in the ore is principally reduced to sulphide, which behaves just like the sulphide of zinc which has remained undecomposed on the calcination of the blende.

Ferric oxide is reduced to ferrous oxide and forms slags with any silica that may be present or with acid silicates. Ferrous silicates combine with any other silicates that may be present to form easily fusible double silicates. They also have the property of dissolving the silica and silicates contained in the material of which the vessels are composed, and thus contribute to the perforation and rapid destruction of these vessels. They also envelop portions of the charge and thus cause any zinc contained in these portions to be retained in the residues. Basic iron slags have the especial property of taking up oxide of zinc and thus withdrawing it from reduction. Lastly, in the absence of silica, metallic iron is reduced from basic iron slags, as also from oxide of iron. Such metallic iron decomposes any other sulphides that may be present with the formation of sulphide of iron.

Oxide of manganese is reduced by carbon to manganous oxide, which forms with silica a very fluid slag. The latter would also envelop portions of the charge. The presence of manganous oxide or silicate tends to the destruction of the vessels, on account of the formation of readily fusible double silicates.

Sulphide of iron is not affected by the processes of reduction. It has an especial injurious action in that it perforates the walls of the vessels.

Oxide of lead is reduced to metallic lead, which is partly volatilised and goes with the zinc into the adapters, and partly remains in the residues. As long as it is not present in too great quantities, and as long as there are only reducing gases present in the retorts, the danger of the formation of silicate of lead, involving the rapid destruction of the walls of the retorts, is not great on account of the ready reducibility of the oxide of lead. If, however, there are large quantities of oxide of lead in the charge, a portion thereof may still remain unreduced at the temperature at which the formation of slag commences, and thus form a silicate. The same action may take place even when lead oxide is present only in small quantity if a considerable amount of air is allowed access to the retort during the course of the distillation. The opinion was formerly held that even small quantities of lead—2 per cent.—cause the rapid destruction of the walls of the retort; but at present it has been proved that the presence of lead in the charge up to 8 per cent. does not notably affect the durability of the retorts. For instance, at Ampsin (Laminne Works) and at Corphalie, ores with 5 to 8 per cent. of lead and 52 per cent. of zinc, and at Bleiberg with 5 to 8 per cent. of lead, are being treated with good results. The retort residues, which contain up to 9 per cent. of lead in the form of small globules, are ground under edge runners, and then jigged, whereby the percentage of lead is brought up to 39. At the Wilhelmine Works, near Schoppinitz, ores with 10 per cent. of lead have been treated without affecting the durability of the muffles.

Lead sulphate is reduced to sulphide, which may react with iron reduced from oxide of iron, so that the greater portion of the lead is separated out, with the formation of sulphide of iron. Any sulphate of lead that has not been reduced may be converted into silicate of lead by the action of silica. Silicate of lead has a corrosive action upon the walls of the vessels. In the presence of any ferrous oxide reduced from ferric oxide, carbon may reduce lead from it, with the formation of ferrous silicate, which also has a destructive action upon the walls of the vessels.

Silicates of alumina have no injurious effect on account of their infusibility as long as other bases are not present. In the presence of bases such as the oxides of iron, manganese and calcium, easily fusible double silicates are formed, which envelop a portion of the charge and attack the walls of the vessels.

Quartz has no injurious action by itself, but if bases such as ferrous oxide, lime and manganese oxide are present, which form easily fusible silicates, it combines with them to form slags, which both envelop a portion of the charge and attack the vessels.

Calcium and *barium sulphates* are reduced by carbon to their respective sulphides, which tend to retain zinc in the residues from the distillation. According to Thum,[1] these substances appear to give off half their sulphur to the zinc in the presence of free zinc and carbon, in accordance with the equation :—

$$2RSO_4 + Zn + 4C = R_2S + ZnS + 4CO_2.$$

Antimoniates are partly converted into antimonides and partly are reduced to antimony, which is volatilised and may pass into the zinc. Sulphide of antimony is decomposed by iron with the formation of metallic antimony and sulphide of iron. *Arseniates* are partly reduced to arsenides, whilst in part arsenic is volatilised from them. A portion of the volatilised arsenic passes into the zinc.

Lime is only injurious in the presence of silica and oxide of iron, these substances tending to produce fusible silicates, the injurious action of which has already been pointed out.

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[1] *Berg. und Hutten. Ztg.*, 1876, p. 145.

Magnesia alone has no injurious effects, but in the presence of silica and oxide of iron likewise tends to form a slag. The presence of considerable quantities of magnesia tends to make the slag difficultly fusible, and thus prevents the absorption of zinc by the latter.

Cadmium oxide is reduced to cadmium and volatilised. Cadmium is more readily reduced and volatilised than zinc, and is therefore deposited with the first condensed pulverulent mixture of zinc and oxide of zinc. It is extracted from this powder.

Any *silver* contained in the charge is only volatilised in very small quantities. The greater portion of it remains in the distillation products, from which it can be obtained by smelting with lead.

The Charge for the Process of Reduction

The charges are prepared by mixing or grinding the ores with the coal used for reduction, no fluxes being added. Formerly lime used to be added to silicate of zinc. It was found, however, that this addition tended to the formation of easily fusible double silicates in the presence of other bases, and has therefore been discontinued. If there are various classes of zinc ore on hand, these should be so combined that a purely siliceous or a purely basic grade is obtained as far as possible. If this is not feasible, they must be so mixed that the silica and the bases shall form a slag as difficultly fusible as possible at the reduction temperature of the zinc, as is the case when large quantities of lime, or, better still, of lime and magnesia, or of alumina, are combined with only small quantities of silica, or, on the other hand, when large quantities of silica exist together with small quantities of the above-named earthy bases. Silicates of alumina are difficultly fusible as long as they have not an opportunity of forming readily fusible double silicates with the silicates of lime, iron or manganese. In the presence of silica, the most injurious substances are the oxides of manganese, iron and alkalies, or any quantity of lead in the ores. The effect of these bodies in the process of reduction should be diminished as far as possible by the addition of zinc ores free from iron, manganese or lead. The ores classified according to these principles are then mixed with an excess of reducing agent. For the latter, lean (non-gaseous) coal is employed as free as possible from pyrites and slate, or else coal that has been carbonised—so-called "*cinder*," or else small coke, or a mixture of raw and carbonised coals. At Freiberg lignite coke is also used as a reducing agent. An excess of the reducing agent is required both in order to bring the particles of ore into the most intimate contact possible with the carbon, and also to promote the formation of a certain quantity of carbon monoxide. The latter gas produces a certain tension in the vessels, which both prevents the passage through the pores of the walls of the vessels, of the gases produced by the furnace fires, which, on account of the carbon dioxide and oxygen they contain, would have an oxidising effect upon the zinc vapours, and also expels these vapours into the condensers and prevents atmospheric air from passing into the latter. When coal is employed, hydrocarbons are evolved, which, in the case of heavy hydrocarbons, are dissociated at high temperatures, causing the separation of a certain amount of carbon, which is deposited in a finely divided state in the charge. This advantage is, however, counteracted by the fact that the expulsion of the gases from these coals requires heat, that the water vapour generated has an oxidising action upon the zinc, and that the zinc vapours are diluted by the expelled gases.

The quantity of the reducing agent has been increased at many works during recent years. For calamine and silicate of zinc, it amounts to from one-third to half of the weight of the ore, according to the zinc contents, and in the case of calcined zinc blende from half to two-thirds of the weight of the ore on account of its difficult reducibility. The grain of the ore and of the reducing material depends on the one hand upon the degree of reducibility of the ore, and on the other hand upon the form of the vessels in which the reduction is carried out. Silicate of zinc is more difficultly reducible than calamine or blende, and as it is only reducible by carbon, and not by carbon monoxide, requires to be brought into the closest possible contact with the reducing agent; both the ore and the reducing agent must therefore be in the finest possible state of division, quite independently of the shape of the vessels of distillation. They should either be ground together or be mixed as thoroughly as possible after crushing. Zinc blende, which is more difficultly reducible than calamine, should also be ground to a very fine powder, say 0·04 to 0·08 inch mesh, as is indeed necessary for its calcination. It must be thoroughly mixed with the reducing agent, which should be crushed to about the same size. Calamine (calcined zinc carbonate) is reduced comparatively easily by carbon monoxide. It therefore requires no such intimate mixture with the reducing agent as does the silicate. If it has to be reduced in vessels of comparatively large capacity, such as muffles, it, together with the reducing agent, need only be crushed to bean or nut size. If it has to be reduced in tubular vessels which possess but a small capacity compared with the muffles, it must be crushed a great deal smaller, as also should the reducing agent. This is required with the object of filling thoroughly the tubes which are very strongly heated by the fire, as well as with the object of avoiding loss of zinc. This loss is partly due to the vessels remaining filled at the end of the process with zinc vapours which burn and are thus wasted when the residues are raked out; the more completely the vessel is filled, the less is the quantity of zinc vapour that can remain at the end of the distillation, on account of the proportionately larger quantity of residues that will be present.

The mixture of ore and reducing agent is either produced by simply mixing the above-named substances in a trough or upon the floor of the works, or else the ingredients of the charge, which have been first crushed separately, are ground together or mixed in pug mills. For instance at Angleur, in Belgium, ore and coal are ground together in a Vapart mill down to 0·06 inch mesh. In order to prevent the ground mixture from being blown away when it is being charged, as also to prevent its being blown out of the tubes by the pressure of the gases evolved in the latter, it is slightly moistened with water. The latter must, however, all be removed before the commencement of the distillation of zinc, otherwise the zinc vapours would be oxidised by it.

VESSELS IN WHICH THE PROCESS OF REDUCTION IS PERFORMED

The vessels in which reduction takes place are nowadays given the shape of either cylindrical or elliptical tubes known as retorts, or prismatic boxes arched above, known as muffles; in England crucibles used also to be employed. These vessels must be made of the most fire-resisting materials possible. The zinc vapours escaping from them are collected in receivers attached to them, made of a less fire-proof material, wherein these vapours can condense to fluid zinc. The gases which pass with the zinc vapours into the receivers or adapters, and which consist substantially of carbon monoxide, pass into an apparatus attached to the adapters in which any metallic portions carried off with them can be retained, whilst the gases are ultimately carried through flues or pipes into stacks. The material of which the vessels are composed, is a mixture of fireclay and burnt clay, or burnt clay and quartz. In some works coke is also mixed with the fireclay. The great objections to these materials is that the clay is a bad conductor of heat, and will not stand great alternations of temperature; that it is attacked by the material of the charge, as also by high temperatures; that it is not quite close in texture but presents numerous minute fissures, and in consequence thereof allows zinc vapour to escape. Steger has therefore recommended the use of muffles made of magnesia bricks:[1] these have not however, come into use up to the present.. The mixture at present used consists of raw and burnt clay, or clean fragments of old vessels in place of the latter, and presents the greater resistance to fluxes, the higher the proportion of alumina as compared with that of silica. For this reason the attempts which have been made, for example in Upper Silesia, to add coarse-grained fragments of quartz to the mixture for making muffles has proved unsuccessful even in the case of basic charges. In Upper Silesia the vessels are made from clays obtained from Saarau, from Mirow, and more recently of clay from Briesen, near Lettowitz in Moravia, which is remarkable for its exceptional fire-proof qualities. The composition of these clays is as follows:—

	I.	II.	III	IV.	V.	VI.	VII.
Locality.	Saarau.	Saarau	Mirow	Mirow.	Briesen.	Briesen.	Briesen.
Authority	Steger [2]	Steger.[2]	Steger.[2]	Steger [2]	Bischof [3]	Hecht [4]	Hecht.[4]
Silica . . .	49·00	50·41	65 39	66·62	44·88	44·87	45·11
Alumina . .	36·75	32·66	22·72	20·82	39·93	39·76	39·68
Ferric oxide .	0·80	3·23	0·91	1·94	0·99	1·14	1·25
Lime . .		0·50		0 51	0·21	0·76	0·07
Magnesia	0·56	—	0·23	0·64	0·08	trace	trace
Potash .	0·41	1·56	0·86	2·20	0·52	0·67	0·66
Soda . .	0·37	—	1·84	—	—	—	—
Loss on ignition .	11·87	11·64	7·77	6·17	13·03	12·95	13·24
	99·76	100·00	99·72	98·90	99·64	100·15	100·01

In Nos. I. and II. 14 per cent. of the silica is in the form of sand, in Nos. III. and IV., 37 per cent., and in Nos. V. - VII., only 0·25 per cent.

The better qualities of fireclay used in Belgium for the manufacture of tubes have the following composition:—

Locality.	Andenne.	Namur.	Natoye.	Natoye.
Silica . . .	54	63	71	76
Alumina	26	24	20	18
Ferric oxide	2	1	2	trace
Lime . . .	—	1	—	—
Water	20	11	7	6

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[1] *Preuss. Minist. Zeitschrft.*, 1894, p. 163.

[2] *Eisen und Metall.*, 1888, p. 53.

[3] Steger, *Zeitsch. d. Oberschles., Berg. und Hütt. Vereins*, 1888, p. 133.

[4] *Thonindustrie Ztg.*, 1888, No. 22.

The following are analyses of certain varieties of clay used in the United States of America:—

Locality.	Woodbridge [1]	Woodbridge.[1]	Cheltenham.[1]	Cheltenham.[1]	St. Louis, Mo.[2]	Perth Amboy, N. J.[2]
Loss on ignition	16·36	16·27	14·65	14·62	13·80	14·30
Alumina	37·32	37·01	30·08	30·47	31·53	35·90
Silica .	42·85	42·83	50·19	50·16	50·80	46·90
Ferric oxide . .	1·18	1·04	2·79	2·48	1·92	1·10
Lime	1·48	1·41	1·31	1·51	-	—
Magnesia	0·41	0·46	0·47	0·29	-	—
Potash . . .	0·76	0·85	0·65	0·97	0·40	0·28
Soda . . .				–	-	0·16
Titanic acid . . .	-	-		–	1·50	1·30

The St. Louis clay contained 12·70 per cent. of the silica as free quartz, and the Perth clay 6·40 per cent.

By the addition of quartz or sand the clay can be made richer in silica, and by the addition of a pure clay-slate, richer in alumina. With ores rich in quartz a certain amount, up to 10 per cent., of quartz may be added to the clay, but in the case of basic ores, it is advisable to employ clay as low in quartz as possible, or to add to clay rich in quartz certain qualities of clay or clay-slate very rich in alumina. As the charge is generally basic, it is in most cases preferable to employ in the manufacture of the vessels a material as rich as possible in alumina and as poor as possible in silica. In the preparation of the material, a portion of the clay is cleaned and dried; another portion is burnt. The burnt and dried clay, as well as the other materials which are to be added, amongst which may be clean fragments of old vessels, or coke, quartz or sand, are ground, generally under edge rolls, and then moistened with water and mixed. The mixing is generally performed in pug mills or by shovelling and treading. The kneaded clay is allowed to lie for a time, usually from 4 to 6 weeks. The proportions of the various materials vary according to their quality. At the Engis Works, in Belgium, the mixture consisted for a long time of 18 parts of coke, 30 parts of raw clay, 27 parts of burnt clay, 15 parts of fragments of old vessels, and 10 parts of sand. At the works in the Rhine Provinces 10 per cent. of coke is used. In many works in Belgium, as also in Spain (Asturias Company, Province of Santander), considerable quantities of quartz or sand are added to clay rich in quartz, so that the vessels consist chiefly of silica. The latter is certainly less resistant towards fluxes than alumina; on the other hand, it stands fire well, is a good conductor of heat, and allows of thinner vessels being produced than does clay. At the works in Upper Silesia, the muffles are made of a mixture of 35 to 45 per cent. of raw clay from Saarau, Lettowitz, and Szczakowa, and 55 to 65 per cent. of burnt clay or fragments of old muffles. From the Lettowitz clay, the composition of which is given above, as also from the clay-shale of Neurode, which contains up to 44 per cent. of alumina, muffles may be made containing 45 of alumina and 53 per cent. of silica, which can resist a temperature of at least 1,800° C.[1] The composition of the Neurode clay-shale is, according to Steger, as follows :—[2]

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[1] *Berg. und Hutt. Jahrb. d. Akad.*, vol. xxvii., Vienna, 1879.

[2] *Eng. and Min. Journ.*, Nov. 25, 1893; *The Mineral Industry*, 1893, p. 650.

	I.	II.
Alumina	36·30	35·70
Silica	38·94	38·29
Sand	4·90	4·40
Magnesia	0·19	
Lime	0·19	trace
Ferric oxide	0·46	1·01
Potash . .	0·42	1·11
Loss on ignition	17·78	19·49

This exceptionally fire-proof clay is burnt twice and cleaned after each burning. This burnt clay makes exceedingly satisfactory muffles. In the United States of North America the muffle mixture consists of equal parts of raw and burnt clay. According to Degenhardt[3] the composition of fragments of Belgian retorts is as follows :—

	Blue Fragments	White Fragments.
Silica . .	41·13	50·10
Alumina .	33·48	38·28
Ferric oxide	2·84	3·42
Zinc oxide	21·47	6·10
Manganic oxide .	0·37	0·41
Lime . .	0·92	1·13
Magnesia . .	0·47	0·73

The receivers or adapters, which are used at present, receive the shape of cylindrical, conical or bellied tubes, or of prismatic boxes arched on their upper sides, which are made of less fire-proof material than the vessels used for distillation. In many places they are composed of equal parts of raw and burnt clay.

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[1] Steger, *op. cit.*, p. 66.

[2] *Op. cit.*, p. 53.

[3] *Ibid.*

To these adapters there are attached nozzles which may take the shape of cones or cylinders made of sheet iron, prismatic boxes made of clay, or prismatic boxes made of clay provided with a grating. These prismatic boxes are connected either with systems of tubes or flues, through which the gases may be conducted into stacks, or with some other apparatus to collect the metallic particles that are still contained in them.

The shape of the furnace depends upon the shape and size of the vessels used for distillation. Those furnaces which contain vessels of circular or elliptical cross-section lying more or less horizontally are called Belgian Furnaces; those in which the tubes stand vertically are known as Corinthian Furnaces; those in which crucibles are used are known as English Furnaces; and those in which muffles are employed are known as Silesian Furnaces. The use of Corinthian and English furnaces has been completely discontinued, and they therefore only now possess an historical value. They will therefore only be considered here in general terms. The Belgian and Silesian furnaces, on the other hand, together with a modification of the former known as Belgo-Silesian furnaces, require detailed description.

The tubes or retorts of the Belgian furnaces are either circular in cross-section, with a diameter in the clear of 6 to 10 inches, and with a length of 3 feet 3 inches to 4 feet 9 inches, or, when the cross-section is elliptical, the long axis is 8⅔ inches in the clear, and the short axis 6¼ inches to 7 inches; the walls are 1⅓ inches thick. The length is limited by the fact that the retorts are only supported at their extremities, and must therefore carry their own weight together with that of the charge without bending or breaking. They lie with one end on projections or ridges along the rear wall of the furnace, and with the other end supported upon ledges of clay in the front wall of the furnace and inclined towards the latter, as is shown in Figs. 47 and 48, in order to facilitate the removal from them of liquid matter and the emptying out of any residue.

Figs. 47 and 48 represent a Belgian furnace with flat grate; *c* are the retorts; *f* are the adapters; *g* the nozzles attached to the latter; *d* are the projections of the rear wall; *e* the clay slabs of the front wall upon which the retorts rest; *k* are plates of cast-iron which form the continuation of these clay slabs; *i* are bricks which support the adapters. The flames generated upon the grate *a* travel round the retorts, ascending in the shaft of the furnace, and escape at *l* out of the furnace proper and pass into the stack. The retorts are disposed in from 5 to 8 rows above each other, so that the greater portion thereof shall be surrounded by the flames. The furnaces are either single furnaces with only one shaft, or so-called double furnaces with two shafts separated by a vertical wall. The muffles of the Silesian and Belgo-Silesian furnaces have the shape of prismatic boxes arched above, as is shown in the cross-section through the front end of a muffle in Fig. 49. The back side is permanently closed, whilst the front side is only closed during the process, the lower half by a clay tile, the upper half by the end of the adapter, or else by a tile which has an opening to receive the adapter. The adapter rests upon a step, which again is supported by projections in the muffle. A muffle with cylindrical adapter is shown in Fig 50. More recently adapters of prismatic form have been used in Upper Silesia. The muffles do not exceed 26 inches in height—usually 24 inches—their width being from 5½ to 6¾ inches; their length varies from 3 feet 3 inches to 7 feet. If the muffle is only supported at front and back, its length must not exceed 4 feet. A big Silesian muffle will take on the average a charge of 2 cwt. of calcined ore. The arrangement of a Silesian furnace fired by means of a grate and with descending flame, being the older type of the so-called Belgo-Silesian furnace, is shown in Figs. 51 to 55. Fig. 51 shows the

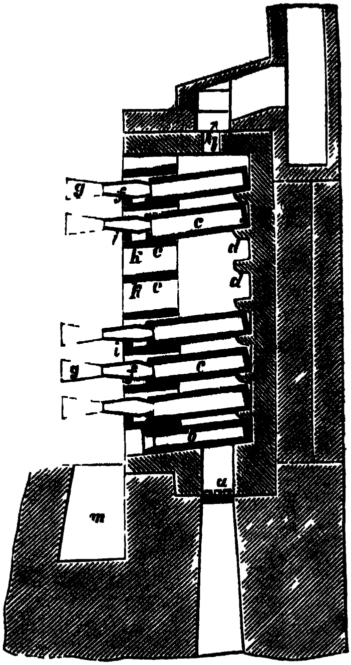
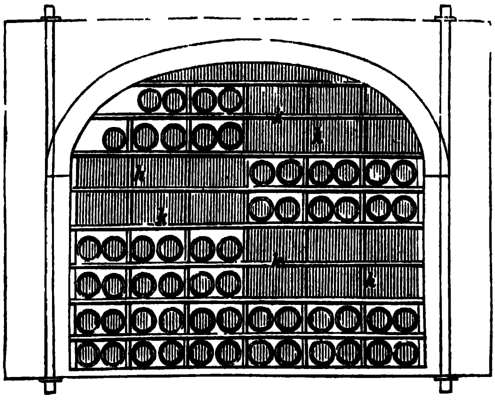


Fig. 47



longitudinal section on the horizontal line *CD*; Fig. 52 a sectional plan on the line *AB*; Fig. 53 a transverse section on the line *EF*. In these figures *e* are the muffles, of which 16 are disposed on either side of the grate; 2 furnaces, with 32 muffles in each, are combined together to form a block. The flame rising from the grate *R* surrounds the muffles *e*, and passes through apertures in the floor of the furnace into the flues *k*, which convey the products of combustion to the stack; *z* is a chamber for calcining calamine or for re-melting zinc; *v* are flues through which the residues from the distillation, which remain in the muffles, are dropped into vaults *T*; these vaults open into a main vault *w*, which runs parallel to the longitudinal axis of the furnace; *u* are the adapters of the muffles, *q* the nozzles attached to these. The zinc collects in the swell of these adapters, and is raked out from them from time to time into an iron ladle held in front of the adapters, the nozzles being removed

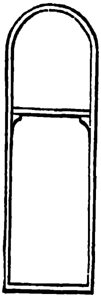


Fig. 49

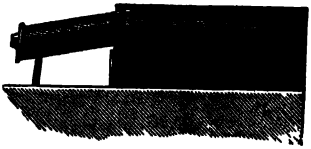


Fig. 50

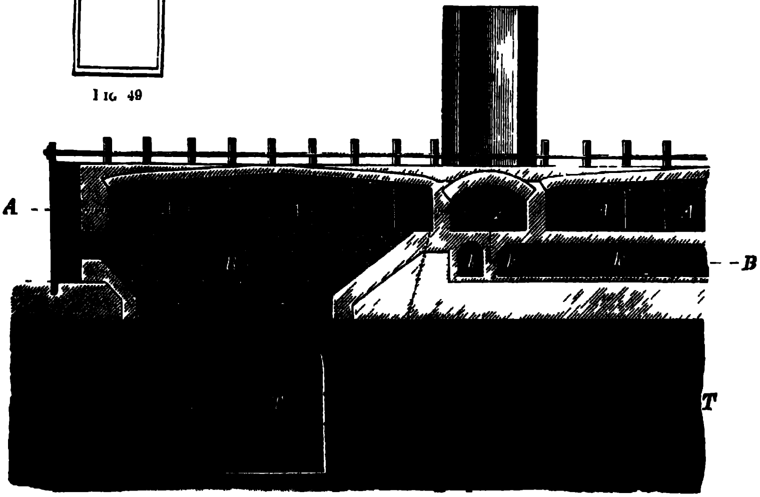


Fig. 51.

for this purpose. The adapters are placed in pairs in recesses into which the front ends of the respective muffles project for a length of about 2 inches. These recesses, of which there are 8 on each longer side of the grate, are separated by party walls *A*. The front of a pair of such muffles is shown on a somewhat larger scale in Fig 54, in which *t* are the steps upon which the back-end of the adapter is

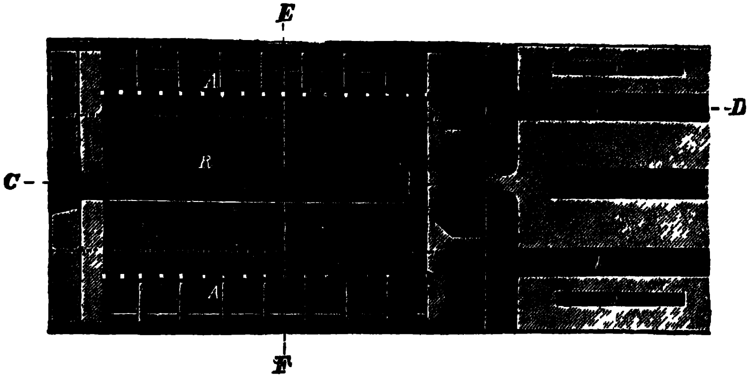


Fig 52

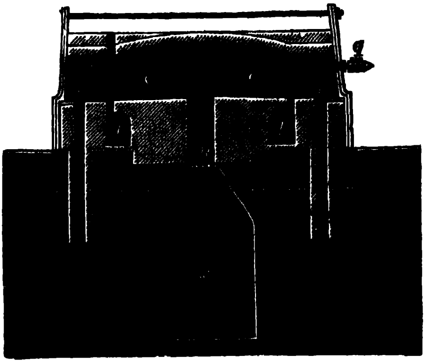


Fig. 53.

supported. The front-end rests upon an iron frame, which is also represented in Fig. 55 upon a somewhat larger scale. The latter closes the recesses in front, and is completely closed below by means of a door *y*.

At some works several rows (up to 3) of muffles are placed one above the other. Such a furnace fired by gas and containing 3 rows of muffles, holding altogether 50 to 55 muffles, which is in use in the Rhine Provinces, is shown in Fig. 56; *m* are the muffles; the two upper rows rest upon benches formed of strongly fireproof clay; *v* are the adapters for the collection of the zinc. The producer gas, generated in a producer not shown in the drawing, passes through the flue *a* into the vertical flue *b*, and is there mixed with the air for combustion, which enters the flue *c* through the flues *l*, and passes

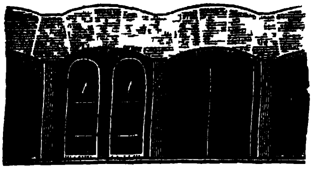


FIG 54

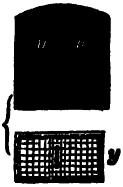
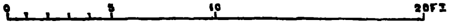


FIG 55



(Scale for Fig. 55)

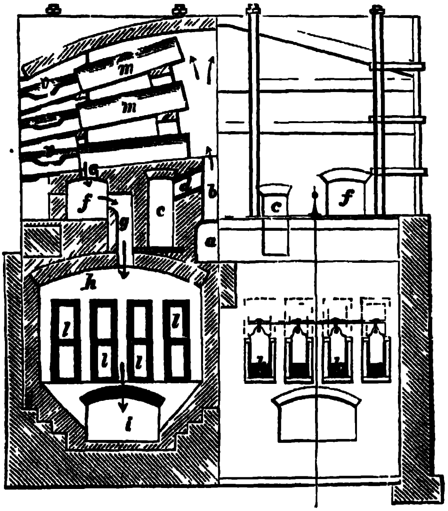


FIG 56

thence through *d* into *b*. The flame rises up to the arch of the heating chamber, then returns and descends through the openings *e* into the flue *f*, whence it passes through flues *g*, *h* and *i* into the stack. On its passage through the flue *h* it surrounds the air flues *l*, by means of which the air used for combustion is heated.

In England[1] the vessels for distillation used formerly to be large crucibles composed of a mixture of 7 parts of best Stourbridge clay, 5 parts of a second-quality clay, 3 parts fragments of glass pots, and 6 parts of fragments of old zinc crucibles. These crucibles were notable for their exceptional durability. Each of them could contain 368 pounds of calcined zinc blende. The crucibles were heated in a furnace arranged like a glass-melting furnace. The zinc vapours, evolved during the process of distillation, escaped through an opening in the bottom of the crucible into a vertical descending pipe. In the latter they condensed and trickled into a vessel of sheet-iron placed at the bottom. The distillation was accordingly a distillation *per descensum*. The construction of such a crucible with its tube attached is shown in Fig. 57. The crucible was charged through the opening on top, the removable cover being taken away for this purpose. These openings were accessible through openings in the vault of the furnace, also provided with covers. The tube for conducting away the zinc vapours was composed of sheet-iron, and was made in two parts, *b* and *c*. The upper portion *b* was held in an iron ring which rested upon a cross piece *d*, welded to the perpendicular iron rods *f*, which pass through eyes secured to the furnace. The iron rods could be raised or lowered in these eyes and clamped in any desired position. By pushing the rods up, the upper portion of the tube, which was provided with a flange, could be brought into close contact with the bottom of the crucible. The lower tube was pushed into the upper one and fastened by being turned round in it. Below the bottom tube there was an iron vessel to collect the zinc. The construction of the English furnace is shown in Fig. 58, in which

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[1] Percy, *Metallurgy*, p. 555.

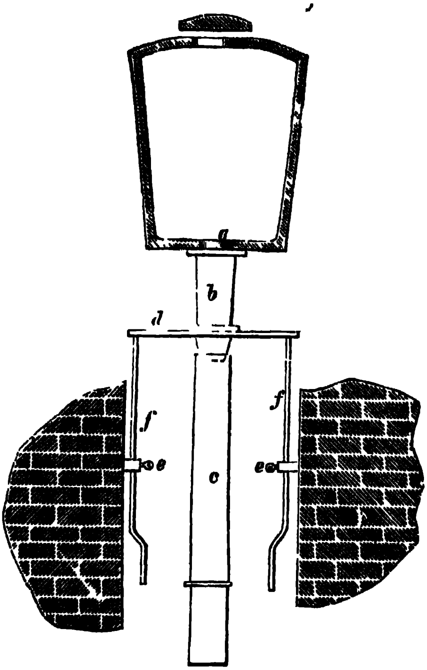

FIG. 57.

e are the crucibles, 6 in number, which were placed on either side of the grate *a*. The flames, after heating the crucibles, passed through openings *g* in the vault of the furnace into the flue; *b* is the fire-door. The crucibles were inserted in the furnace through arched openings *m*, which were closed during the operation by means of movable walls built of brick lumps. In the latter there were small openings *c*, which could be more or less closed as required by means of bricks, the fire-door being kept closed by means of a shovelful of coals. The openings *c* served to clay up any cracks in the crucible that might form in the side exposed to the fire. The crucibles were charged through the openings *h*, which were kept closed during the operation by means of a tile *i*. The gases escaped through the aperture *g* into the flue, a tile *l* being used for regulating the draft; *f* is the tube through which the zinc vapours were conducted down, *p* the sheet-iron vessel in which the condensed zinc was collected. The residues after distillation were removed through the opening in the bottom of the crucible. These English furnaces have been entirely disused, and have been replaced by Belgian or Silesian furnaces on account of their high consumption of fuel, one ton of zinc requiring from 22 to 27 tons of coals.

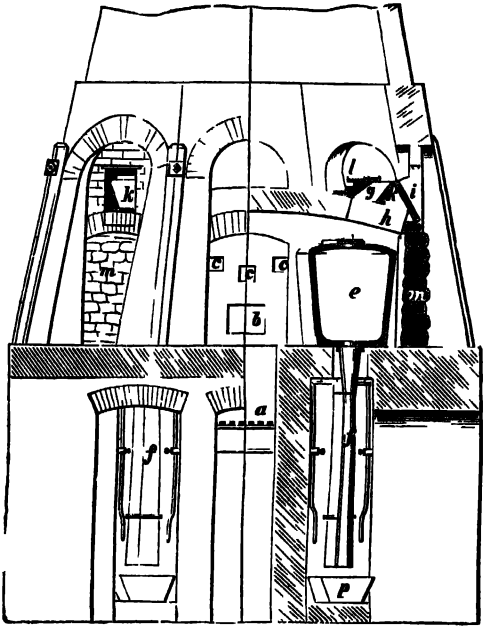

Fig 56

At Delach, near Greifenburg, in Carinthia, small vertical tubes were used at the commencement of this century in the process of distillation.[1] These tubes were closed at their upper wider end, and opened at their bottom end into a tubular receiver through which the zinc vapours passed into a chamber common to all the tubes, in which they were condensed. The floor of this common receiver was formed by an iron plate upon which the zinc trickled down. Eighty-four such tubes were placed in a reverberatory furnace. The tubes were 3 feet 3 inches long, 4⅛ inches in diameter at the top, and 3¼ inches at the bottom. From 5 to 7 lbs. of ore were charged into each, the upper empty portion of the tube, 4 inches long, being filled with small pieces of charcoal. This method of distillation has long been abandoned on account of the high costs connected with it. Recently vertical tubes of larger diameter for the treatment of lead-bearing zinc ores have been proposed by Chenhall,[1] by Binon and Grandfils,[2] by Keil,[3] and by Grutzner and Köhler.[4] The furnace of Binon and Grandfils, which possesses such tubes arranged for continuous working, with adapters to collect the zinc at their upper ends, and with an opening at the lower end for the removal of the residues of distillation and for the collection or tapping off of the lead, is shown in Fig. 59. *D* is the tube 8 feet 10 inches long and 15¾ inches in diameter. It stands in a cast-iron tube *E* filled with clay, which is attached to the upper portion of a boot-shaped projection *F*. The upper opening of the tube, through which it is charged, is closed by means of a cover *b*. *K* is a conical adapter for the collection of the zinc vapours. Each furnace contains 12 to 16 of such tubes, which stand upon the cast-iron boxes *F*, which in their turn are supported by the brick pillars *G*. The tubes are heated by gas, which is burnt in the flues *H* by the aid of air previously heated. Nothing is known to the author as to the practical results obtained in these tubes or their application on a large scale.

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[1] Hollunder, *Tagebuch einer Met Reise*, Nurnberg, 1824, p 273, Percy, p 585.

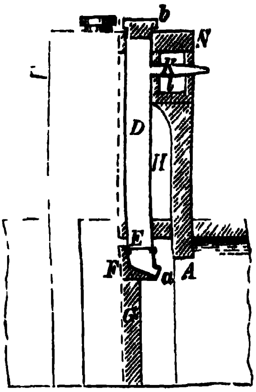

Fig. 59.

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[1] *Oesterr. Zeitschr.*, 1880, p. 462.

[2] *Ibid.* 1881, p. 325; *Dingl. Journ.*, vol. 235, p. 222.

[3] *Berg. und Hutt. Ztg.*, 1888, p. 116.

[4] D. R. Patent, No. 58,026, September 25, 1889.

GENERAL CONSIDERATIONS RESPECTING THE PROCESS OF REDUCTION

As will be seen from the above statements, the process of reduction is carried on in comparatively small vessels more or less readily destroyed, which do not admit of continuous action, and are expensive to produce, whilst the cost of fuel and wages is high. If to this is added that the extraction of zinc is an imperfect one, ranging from 70 to 90 per cent. of the zinc contents of the ore, because the losses of zinc amount, under the most favourable circumstances with rich ores, to 10 per cent. of the contents of the ore, and in the case of poorer ores to 30 per cent., being due to zinc remaining behind in the residues, to zinc vapours that remain in the vessels at the end of the distillation and the burning of the latter when the residues are removed, to imperfect condensation of zinc vapours, to the escape of zinc vapours from the vessels, and to the retention of zinc as an aluminate in the walls of the vessels, the present process of zinc extraction must be considered as a highly imperfect one, when compared with the processes for the extraction of metals which are not volatile when reduced in the dry way. In consequence of the above-named difficulties, poor zinc ores cannot be utilised at all for the extraction of zinc. It is therefore intelligible that metallurgists have long been striving to replace the present discontinuous process by a continuous process in shaft furnaces. The whole of the attempts in this direction have, however, as far as regards the extraction of metallic zinc, given unfavourable results. Having regard to the difficulty of the condensation of zinc in vapours which are diluted to a high degree by the products of combustion and by the nitrogen of atmospheric air, such as is the case with zinc vapours obtained from shaft furnaces, it is not probable that the problem of the direct extraction of zinc in such furnaces will be satisfactorily solved. It is, however, highly probable that ores poor in zinc may be worked in shaft or reverberatory furnaces and yield intermediate products rich in zinc, as, for instance, mixtures of pulverulent zinc with small quantities of oxide, or zinc oxide, which would form a suitable material for zinc distillation in appropriate vessels.

Having regard to the small probability of success in the direct zinc extraction in shaft or reverberatory furnaces, efforts during the last 20 years have been directed to the improvement of the process of zinc extraction in its actual form, with favourable results. These improvements consist chiefly in the introduction of gas-firing, in increasing the size of the furnaces, in improving the fire-proof qualities of the material employed for the vessels, and in the production of these with dense walls by the employment of hydraulic pressure, the improvement of the apparatus used for the condensation of zinc vapours, and for the removal of condensed zinc from the adaptors, for the collection of the zinc which has not been condensed in these, and for keeping the interior of the zinc works free from fumes. We have therefore to consider as the only method of zinc extraction used up to the present in the dry way, the distillation of zinc in vessels and its chief variations:—

(1) Distillation in horizontal retorts or the Belgian method.

(2) Distillation in muffles, or the Silesian method.

The other above-named methods, viz., the English and the Carinthian, are no longer in existence, and need therefore no further consideration.

COMPARISON OF THE PROCESS OF DISTILLATION IN RETORTS AND MUFFLES

The differences between distillation in retorts and in muffles have been pretty well equalised since the introduction of gas-firing. There are districts in which distillation is carried on in retorts to as much advantage as it is in muffles, as for instance the Rhine Provinces, Westphalia and Belgium. As long as ordinary grates only were used for zinc distillation, the choice between retorts and muffles depended generally upon the flame-giving quality of the coals. Distillation in retorts required coals giving a long flame. whereas distillation in muffles could be performed also with coals that gave but a short flame. Only in recent times has it been rendered possible by means of special construction of grates to use fuel giving a short flame also for the heating of retorts. For example, in the United States by burning anthracite coal upon what are known as Wetherill grates, consisting of cast-iron plates with conical holes, by means of heated air, a long flame suitable for the heating of retorts has been obtained. Hence it happens that in districts which yielded coals giving short flames, as in Upper Silesia, muffles were first employed, whereas in districts in which fat or long-flaming coals were available, as in the Rhine Provinces, Westphalia and Belgium, both retorts and muffles came into use. By the introduction of gas-firing in its various modifications, and of the above-mentioned Wetherill grates, the choice of the vessels employed has been rendered independent of the flaming properties of the fuel.

Retorts present the objection that, being only supported at their two ends and completely exposed to the fire, they last for a shorter time than do muffles, and therefore necessitate a greater consumption of fireproof material, and this of better quality than do muffles. Their capacity at the same time is less than that of the muffles, so that they require to be more frequently filled and emptied than do the former. For these reasons, and also on account of their being disposed in a large number of tiers one above the other, they require more highly skilled labour than muffles, so that the cost for labour in working them is greater than in the case of muffles. When fire-grates are used, they require, however, less fuel than muffles; when gas-firing is used, and when the air needed for combustion is first heated, or when both air and gas are heated, any difference in the consumption of fuel disappears, especially when several rows of muffles are placed one above the other. On account of their smaller diameter and their free position in the fire, heat penetrates more rapidly into the interior of the retorts than into muffles. They are therefore specially useful for difficultly reducible ores which require a very high temperature like silicates of zinc. On account of their small capacity they have to be filled very closely, and are therefore suitable for ores crushed very fine, as, for instance, roasted blende. For the treatment of poor ores, retorts are less suitable than for the treatment of rich ores, because the former require a longer time for their reduction, and are therefore best treated in muffles, in which the ores remain twice as long as they do in retorts. For example, in Belgium, ore containing less than 35 to 40 per cent. of zinc cannot be treated with advantage in retorts, whereas in Upper Silesia ores containing 12 per cent. of zinc are treated successfully in muffles. Since the introduction of gas-firing, and since muffles have been placed in several tiers one above the other, it is no longer possible to give a general decision applicable to all instances regarding the choice of muffles or retorts. Both forms of vessels are used with equal advantage in many districts for both calamine and blende. For example, in Belgium retorts are used at Angleur, Corphalïe and St. Leonard, whereas muffles are used in Flône and Valetin Cocq. In the Rhine Provinces retorts are used at Muhlheim and Moresnet, muffles at Borlech, Hamborn and Stahlberg; in Westphalia muffles are at present employed; in Upper Silesia muffles are used exclusively; in Spain and in the United States only retorts.

Very difficultly reducible ores, such as silicate of zinc, are best treated in retorts—poor ores in muffles. Finely ground ores, as also ores rich in zinc, may be treated in retorts or small muffles (Belgo-

Silesian muffles), which are placed in several rows one above the other, when good and cheap fire-resisting material is obtainable, and when labour of sufficient skill is available, whilst under opposite circumstances large Silesian muffles should be employed. Coarse-grained ores can be treated both in muffles and in retorts; it depends upon their zinc contents which form should receive the preference. Poor ores are best treated in Silesian muffles, rich ores in retorts or Belgo-Silesian muffles.

The question how poor an ore may be and still be treated profitably, depends, apart from the price of zinc, upon the rate of wages, the cost of fuel, and the cost of fire-resisting materials. The item of coal is the highest, next comes that of wages, and lastly that of fire-resisting materials. For example, the costs of distillation per ton of calcined ore in Belgo-Silesian furnaces, under conditions obtaining in the Middle Rhine Provinces, are distributed as follows, according to Lynen:—[1]

Coals	15s.
Wages	12s.
Fire-resisting materials	6s
Maintenance and General Expenses	7s

It has already been stated that Belgian ores containing much under 40 per cent. of zinc can no longer be treated with advantage in retorts, whilst in Upper Silesia calamine with 11 to 12 per cent. of zinc can be worked in muffles.

As the outlay for coals forms the chief item in the cost of zinc extraction, zinc works should as a rule be erected in the neighbourhood of coal-mines, and the ores should be carried to the coals, not the coals to the ores. For 1 part by weight of zinc 4 to 10 parts by weight of coal are consumed.

I. THE BELGIAN METHOD OF ZINC DISTILLATION

As already stated, this method of distillation is performed in retorts lying at a flat angle of inclination and heated in externally-fired shaft furnaces. The zinc vapours thus formed are condensed in conical adapters provided with nozzles.

The tubes or retorts are made of the shapes and dimensions already given; quite recently the walls have been made only ¾ inch thick, the material consisting chiefly of silica similar to Dinas brick. At La Salle, Illinois, U.S.A., retorts have been used rectangular in cross section and of large dimensions, which have to resist the first attack of the flames, the firing being by gas; their outside dimensions are 5 feet long, 20 inches high, and 9 inches wide.

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[1] *Zinc furnace with common condensing chamber*, London, 1893

The material of which the retort is made has already been referred to. The mixtures employed at the different works vary greatly and depend upon the contents in quartz and alumina of the various materials that are obtainable, as also upon the nature of the gangue of the ores. In many works finely ground coke is added to the materials employed in order to make the retorts firm, smooth, and impenetrable to zinc vapours. Retorts made from material rich in quartz are glazed for the same purpose with a glaze consisting of 60 parts of loam, 30 parts of glass, and 10 parts of soda. If the mixture contains too great a quantity of raw clay, it becomes less fire-resisting; if it contains too much burnt clay, it is difficult to mould, and the tubes become porous and brittle. For example, the mixture used for retorts at the Engis Works, in Belgium, for a long time consisted of 30 parts of raw clay, 27 parts of burnt clay, 15 parts of old retorts, 18 parts of coke, and 10 parts of sand. Another mixture used in Belgium for retorts made by machinery[1] is as follows:—

	Parts by Volume.
Coke	100
Sand .	300
Old Retorts .	250
Raw Clay .	350

In England, at Morriston, the mixture for retorts, cooled by a current of air, consists of 1 volume of raw Belgian clay from Andenne, 2 parts of burnt Belgian clay, 1 part of raw, and 1 part of burnt Stourbridge clay, all by volume, or else 1 part by volume each raw and burnt Belgian clay, raw English clay, fragments of old retorts, and Belgian sand. For ordinary retorts, the mixture is 1 part by volume of Belgian clay, 1 part of English clay, 3 parts of old retorts, or 1 part of Belgian clay, 1 of English clay, 1 of burnt Belgian clay, 1 part of old retorts, and 1 part of old fire-bricks. In the United States of North America equal parts of fresh and burnt clay are used. The latter may consist of either clay freshly burnt or of the fragments of old retorts. A mixture of quartzose material which has been quite recently employed has the following composition: one-third clay from Andenne with 60 to 70 per cent. of silica, one-third sharp-edged sand, and one-third burnt clay. The mixture contains 94 per cent. of silica.

The above materials are first crushed, then kneaded together

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[1] Knab, *Metallurgie*, p. 431.

to a uniform mass, with the addition of 7 to 8 per cent. of water. Crushing is performed by means of edge runners, Carr's disintegrators or Vapart's disintegrators. The latter apparatus, generally used in Belgium, will grind from 3 to 3½ tons per hour. If the grain is too coarse, the retorts will be porous; if, on the other hand, it is too fine the retorts readily soften in the fire. The clay is ground to a fine flour, whilst burnt clay and fragments of retorts are passed through a sieve of 0·2 inch mesh, but the average grain of the whole does not, as a rule, exceed 0·12 inch. The materials are kneaded together in an ordinary pug mill, and only exceptionally by hand. After kneading, the mass is usually allowed to lie from 6 to 8 weeks in cellars to make it more plastic; it is then cut up into lumps The manufacture of retorts may be performed by hand or by machine, machines being mostly employed, hand work having been given up at present at most works. Retorts when made by hand are mostly made by means of sheet-iron moulds, which consist of several sections: each section consists of two halves, each of which has the shape of a hollow semi-cylinder. The two faces are then placed together, when they form a cylinder, and are kept together by means of rings and wedges. Into the bottom part of the mould a disc of clay is placed, which is then hollowed by means of a stamper to form the bottom of the retort, so that the edges of the disc rise up to form the commencement of the walls of the cylinder. The portion of the disc that has been forced up is now beaten against the wall of the mould by means of a beater and then scraped and smoothed out by the help of a sweep. The upper edge of that portion of the retort that is thus produced is then scored with a comb-shaped board, when it can be lengthened to the required extent by the addition of rings of clay. As soon as these rings have reached a certain height, the cylinder thus formed is surrounded by a new segment of the mould. The clay is once again beaten against the wall of the segment that has been put on, and is again bored out by the help of the sweep. The upper edge of the tube thus prolonged is again scored, and the previous process is repeated, and continued until the retort has reached the desired height. A small ring of clay is then placed upon the top edge and pressed inwards in order to strengthen the wall of the retort at this point. Finally the upper edge of the retort is cut smooth. It, together with the inside of the retort, is planished, and the whole is then placed in a well-ventilated room. A workman can produce from 18 to 20 retorts in 12 hours. After some 48 hours the various segments of the mould are removed gradually and the retort is then allowed to stand for another three weeks until it is completely air-dried. It is then dried for two or three months in chambers heated by furnaces or stoves to a temperature of 25° C. at first, rising ultimately to 70° C. The longer the retorts are allowed to remain in these heated drying chambers, the better do they stand in use. Another method of manufacturing retorts by hand consists in placing a cylindrical core into the mould and stamping the material of which the retort is to consist into the ring-shaped space left between the mould and the core.

The manufacture of retorts by machinery is performed in various ways. The older method, which is still in use at Angleur, in Belgium, consists in forcing the clay wrapped in linen into a vertical, cylindrical, or elliptical wooden mould arranged to open, and then boring out, by means of a drilling machine, a cylindrical or elliptical hole in it. The clay is stamped in by means of a hammer moving up and down. After the mould has been filled in this way it is carried with its contents to the boring machine, which then hollows it out. The mould is then opened, and the retort is taken out and carried into the drying chamber, where its linen covering is removed, and where the inside is smoothed. At Angleur three men and two boys can make 140 retorts in this way in 10 hours.

A second method, which is now used at most of the Belgian zinc-works, consists in first moulding the clay into the form of solid cylinders, and then pressing these into the shape of retorts by hydraulic machinery. By these means the bottom of the retort is made in one piece with the tube. The solid cylinders are 1 foot 8 inches in diameter, and 2 feet in length. They are produced by pressing lumps of clay into cylindrical or elliptical moulds, the bottom of which is formed by a hydraulic piston. After the clay has been rammed sufficiently firmly into the mould with hammers, it is forced out of the mould by means of the hydraulic ram, and then, by means of hydraulic presses, forced into the shape of the retort. There are various forms of these hydraulic retort machines in use. One of them consists of a vertical cylinder of cast steel, the interior of which has the shape and dimensions of the exterior of the retort. Inside it there is a hollow core of the shape and size of the interior of the retort to be moulded. A lump of clay is first thrown into the cylinder to form the bottom of the retort. The upper end of the cylinder is then closed, and by means of a hydraulic ram a pressure of from 150 to 200 atmospheres is exerted upon the clay in the cylinder, from beneath. The bottom is formed by pressing the clay against the cover of the cylinder, the walls by the clay being forced into the annular space between the cylinder and the core ; the pressure is kept on for some 2 minutes. After this, the cover of the cylinder is taken off, and the retort is forced out of the mould by allowing the hydraulic cylinder to rise. When it has reached the desired length, the retort is cut off by means of a wire. Another form of moulding machine consists of a vertical hollow cylinder of cast steel, in which there is an annular piston which fits exactly into the interior thereof. Inside the annular piston there is a cylindrical core of the shape of the interior of the retort; both pistons work from below upwards. The top of the cylinder is closed by a heavy cover of cast steel. To make a retort, a cylindrical block of clay of the requisite size is introduced into the cylinder, the top of which is closed. Both pistons are at first pressed simultaneously upwards to compress the clay, thereupon the inner cylinder or core is forced into the clay, whilst the annular cylinder sinks back. By this movement the retort receives the shape required. After it has been formed, the upper end of the cylinder is opened, and by forcing up the annular cylinder the retort is pressed out of the apparatus; here also the pressure amounts to 150 to 200 atmospheres, and is applied for some 2 minutes. A machine of the first kind is used, for example, at Ampsin in Belgium. This machine will make 145 retorts in 10 hours, with the labour of 4 men per shift. Another man is required for moulding the clay cylinders, and another removes the finished retorts into the drying-house. A machine of the second class is in use at the Munsterbusch Works, near Stolberg, for the manufacture of muffles; 145 to 150 muffles are there produced in 10 hours, three men being required. Retorts manufactured by the aid of hydraulic machinery are better and more durable than those produced by hand, especially because the walls are denser, so that the loss of zinc has become considerably less since they have come into use. Retorts made by machinery are dried in the same way as those made by hand. Before the retorts are introduced into a furnace in operation, they must be heated for a time in a kiln to prevent their cracking and bending. They must be heated up to a red heat for 12 to 24 hours, and must be turned round at half time.

The kilns, in which the retorts are heated before being used, are reverberatory furnaces, through the beds of which pass numerous perforations. The retorts are placed in the heating chamber above this bed. The grate is either below the perforated bed, so that the flames pass through the openings in the latter from below upwards, or else it is on one side, and the flame passes over a fire-bridge into the upper part of the heating chamber, passing through the latter from above downwards, and escaping through the openings in the hearth into the flues. A furnace of the latter kind, which is said to have done exceedingly good work, and to have been very durable, and which is preferred in England to kilns of the first kind, is shown in Figs. 60 to 62. *A* is the heating chamber, 7 feet long, 4 feet 6 inches wide, and 5 feet high in the centre, holding some 25 retorts; *a* is the fire-place; the grate, 4 feet 3 inches long and 12 inches wide, consists of two halves inclined towards each other; *b* is the fire-bridge over which the flame passes into the heating chamber. The flame traverses the latter from above downwards, and passes through the apertures *c*, 4 inches square, in the bed, into the flue which leads the products of combustion into the stack.

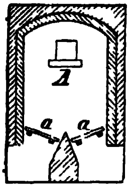

Fig. 60

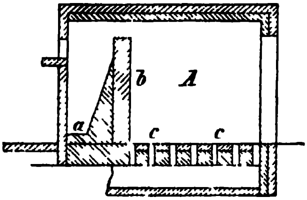

Fig. 61

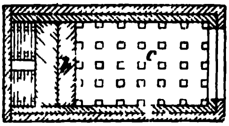

Fig. 62

Adapters

The adapters in which the gaseous zinc condenses, are short conical tubes of clay, which is, however, less fire-resisting than the clay of the retorts. They are usually composed of a mixture of equal parts of raw and burnt clay. In England the mixture consists of one part of clay from Andenne, one part of Stourbridge clay, and four parts of old retorts and bricks. The mixture is either formed into sheets and turned round cores and then beaten firmly against the latter, or else it is pressed into a conical metal mould, into which a core is forced. The piece thus made is carefully dried, smoothed inside, and finally burned. These adapters are about 16 inches long, 6 inches in external diameter at the wide end, and 3 inches at the narrow end. A workman can make 100 of these in a day. Before being used, they are coated with milk of lime in order to be able to remove without difficulty any accretions that may form in them. The wide end of the adapter fits into the retort, the space between the two being filled up with clay. An adapter lasts from 8 to 10 days. The fragments of old adapters after being cleaned can be used for the manufacture of firebricks of inferior quality. The mode of attaching the adapter, and its position with respect to the retort are seen in Fig. 63, the wide end of the adapter being luted to the retort *r*; the front narrow end rests upon a brick. To it is attached the so-called nozzle, which is made of sheet-iron, and serves to catch any particles of metal that may be carried off by the vapours; it is secured by means of wires, which are made fast to the front wall of the furnace.

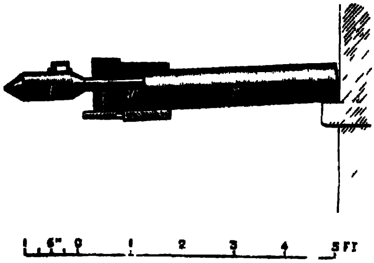

Fig. 63.

Furnaces

The furnaces employed in distillation are, as already mentioned, shaft furnaces fired externally. The retorts are disposed in them in a number of tiers one above the other so that the greater portion of their surface shall be exposed to the flame. The number of retorts which a furnace will take varies, according to the dimensions of the latter, between 50 and 400. For example, a double furnace in La Salle, in the State of Illinois, has on either side 204 retorts, or 408 altogether. At Angleur double furnaces carry 100 retorts in 5 rows of 20 each on either side, those at Ampsin 50 in 5 rows of 10 each ; at Corphalie 7 rows of 10 each, 7 rows of 12 each, and 6 rows of 10 each on either side; at Bleiberg 70 and 84 retorts on either side. In order to enable the furnace to hold as many retorts as possible they have been made oval in cross section, or the front of the furnace has been made of hexagonal frames of cast iron, the end of a retort fitting into each hexagon, or instead of the hexagons cast-iron rings have also been employed. The furnaces are either single, and then consist of one shaft-like chamber filled with retorts, or else are double, in which case they are divided by a vertical partition wall into two shafts, each of which carries retorts. With respect to the mode of firing, furnaces are divided into those fired by means of grates, those fired by grates and gas, and those fired by means of gas. By a suitable modification of grate firing (Wetherill grates and modified gas-firing), and more especially by the introduction of gas firing, important advantages as regards the consumption of fuel and economy in retorts have been attained, and the distillation has been rendered independent of the nature of the fuel. Unless, therefore, under exceptional circumstances, the method of gas firing should as a rule be used for Belgian furnaces. We have accordingly to consider :—

1. Furnaces fired by grates.
2. Furnaces fired by grates and by gas.
3. Furnaces fired by gas.

1. *Furnaces Fired by Grates*

These furnaces are either single or double. The grates are either flat or step-grates. When long-flaming coals are available, the so-called clinker grate is used, in which the fresh coals are thrown upon a bed of clinker, and the air which enters under the grate is warmed by passage through this bed. The clinker is removed through the interspaces between the grate bars, and falls into the ashpit. A clinker grate has the advantage, as compared with ordinary grates, of consuming effectually the fuel, of heating the air used for combustion, and of only needing the removal of ashes at longer intervals of time, as also of affording a better protection to the grates against the fire. For leaner coals the so-called open grate is used in which ashes are removed from above. Anthracite can be burned on the so-called Wetherill grates. These are in use in Bergen Port and in Bethlehem in the United States. The grates consist of cast-iron plates 1⅛ inches thick, which are pierced by conical holes. These holes are 1 inch wide at their wide end, 0·4 inch at the narrow end. There are 100 holes to the square foot. The plates are so arranged upon cast-iron bearers that the narrow ends of the holes are uppermost, thus preventing them from becoming stopped up. Air is introduced by means of a fan blast and conducted by means of a flue passing underneath the floor of the works into the closed ashpit. A further portion of air is heated in the lowest retorts, which are not charged, and is conducted into the fireplace. By this means 7 tiers of retorts can be heated.

Single Furnaces

In these furnaces 11 to 12 retorts are allowed to every 35 cubic feet of furnace capacity, and 1 square foot of grate area to 16 to 20 cubic feet of furnace capacity. The older Belgian furnace—the so-called Liège furnace—was designed in 1807 by Abbé Dony in Liège. Its arrangement, as it was erected at Moresnet, is shown in Figs. 64 and 65.[1] The arched furnace shaft is 10 feet 6 inches high, 8 feet wide, and 5 feet deep. It contains 69 retorts in 9 tiers. The lowest tier of 8 retorts, which lie nearest to the grate, known as *protecteurs*, or "*cannons*," is not charged. Their only object is to weaken the cutting action of the flame and to distribute the latter uniformly amongst the other retorts. The remaining retorts are arranged with their back ends upon the projections *v* of the back wall, and with their front ends, in the 6 lower rows, resting upon tiles (*taques*), *s*, the prolongation of which is formed by plates of iron; in the two upper rows they rest upon plates of iron only. By means of bricks placed on edge the whole front wall of the furnace is divided into compartments, which contain in the topmost row one retort each, whilst in the lower tiers they contain two retorts each. *R* is the grate, *M* the fire door, *N* are

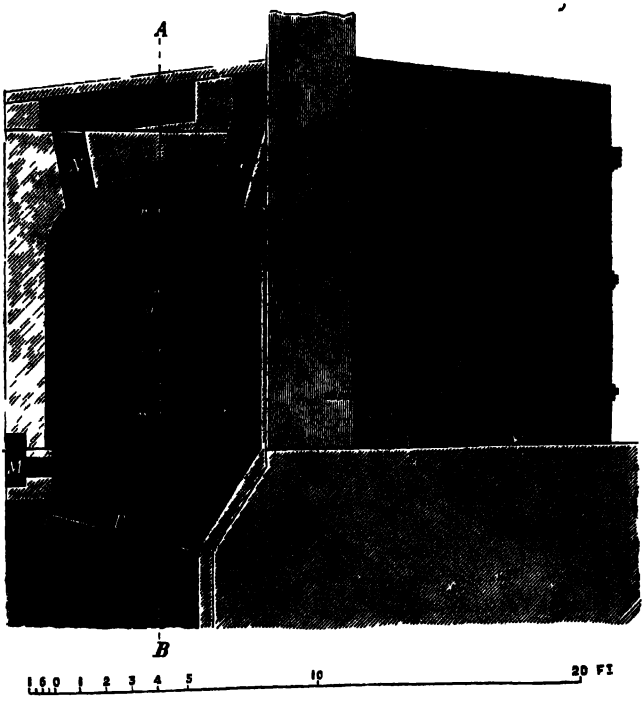

FIG 64

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[1] *Berg. und Hutt. Ztg.*, 1859, p. 405; 1860, p 3.

the flues, through which the products of combustion escape either into the stack or into the furnace for calcining calamine. *K* is a chamber in which the residues from distillation are collected. The arrangement of the retorts and adapters is shown in Fig. 66 At the Morriston Works of Vivian and Sons, near Swansea, in England,[1] there were in 1878 single Belgian furnaces in use, the larger of which contained 6 tiers of retorts, 16 in a row and 1 tier with 16 blanks, or 112 retorts altogether. The blank retorts or "*cannons*" were constructed with an air flue in their lower portion in order to cool them, as shown in Fig. 67. Each furnace had two fireplaces 6 feet long by 9 inches wide. Each furnace treated two charges daily, but the four bottom tiers only treated one charge each. In 24 hours 27 cwts. of calamine and blende, containing 50 to 51 per cent. of zinc, and 15 cwt. of coal-dust,

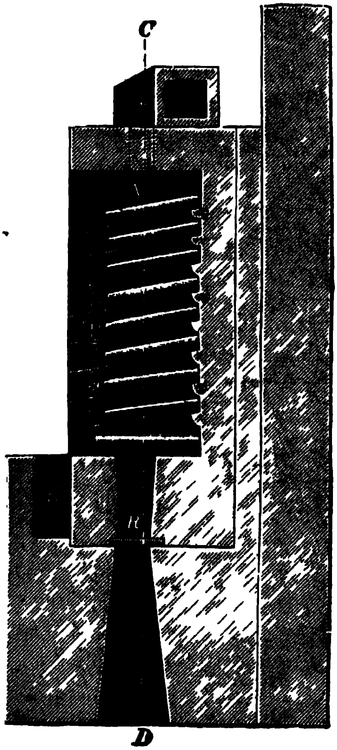

FIG 6

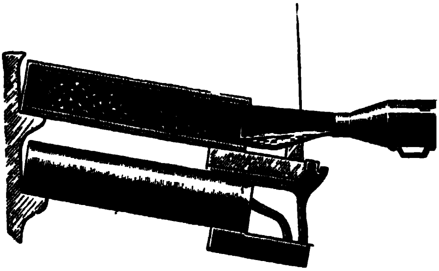

FIG 66

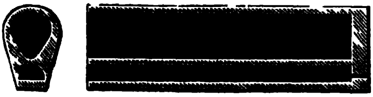

FIG 67

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[1] Borgnet, *Berg und Hütt Ztg*, 1878, p 388

were distilled, the product being 11 to 11½ cwts. of zinc. The coal consumption was 2 tons to 1 ton of ore. There were three men employed on each shift. Four retorts were destroyed in every 24 hours. These furnaces were not satisfactory as regards the consumption of fuel and the working costs, and were far surpassed by the Cornwall furnace employed at the same works, designed by Alfred Borgnet.

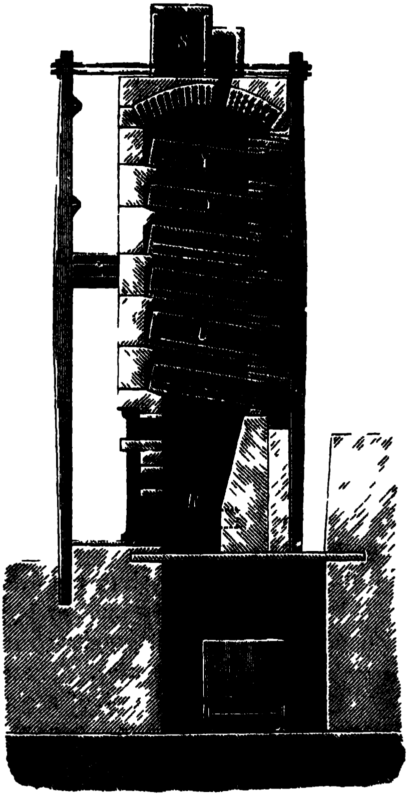

Fig. 68

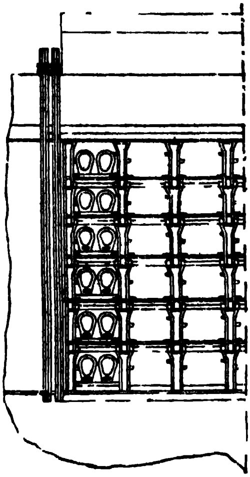

Fig 69

Instead of one single grate running parallel to the longitudinal axis of the furnace, these furnaces possess five grates at right angles to the axis, inclined parallel to the direction of the retorts, and capable of being fired from the back side of the furnace. In consequence of this arrangement, the length of the furnace can be notably increased. The construction of these furnaces at the Morriston Zinc Works is shown in Figs. 68 and 69. They contain 120 retorts in 6 horizontal tiers. The retorts *U* of the four lower rows, the so-called *cannons*, have air flues as shown in Fig. 67, whilst the retorts of the two uppermost tiers are without such flues. *R* is one of the five grates 24 inches by 6 inches in area. The products of combustion pass through seventeen apertures in the arch of the furnace into the main flue *S*, and from the latter into a stack 23 feet in height. The front wall is composed of 11 cast-iron pillars, cast in one piece, each of which is 4 inches broad, and has walls 0·4 inch thick. The interspaces between the walls are filled with fire-proof material. Cast-iron plates 1 foot 8 inches long slide in grooves along the pillars, and upon these lie firebrick tiles, upon which the front portions of the retorts may rest. The length of the furnace between the outer walls, which are 4 feet thick, is 20 feet 6 inches, the width, including the brickwork, is 7 feet, the height from the grate to the arch is 14 feet, the height in front from the first cast-iron plate to the spring of the arch is 10 feet. The distance between the cast-iron plates of the first and second tiers amounts to 20 inches, of the third and fourth tiers to 19 inches, of the fifth and sixth tiers to 17 inches. The recesses are 20 inches wide, and carry two retorts each. The arch consists of alternate layers of the best firebrick and Dinas brick, and is 10 inches thick. The furnace is supported upon iron rails. It is capable of treating 2 tons 2 cwts. of ore containing 49 to 50 per cent. of zinc, mixed with one ton of coal, in 24 hours, the output being 15¾ to 17 cwt. of zinc. For 1 ton of ore 2 tons of fuel and 1·6 retorts are consumed. There are three men on the shift.

The Belgo-Cornwall furnace[1] contains four tiers, each of ten oval *cannons* or dummy retorts, and two rows of nine retorts each, or 108 retorts altogether. The grates are not transversal, but longitudinal, there being two, each of 8 feet 6 inches by 10 inches area. These furnaces treat in 24 hours 30 cwt. of ore mixed with 9 cwt. of coals, with an output of 12½ to 13 cwt. of zinc. Each ton of ore requires the consumption of 42 cwts. of coals as fuel. A furnace destroys four retorts per day. Compared with the older Liége furnace the Cornwall furnace requires less labour and is far more durable, lasting five to six years, as compared with twelve to fifteen months. On the other hand, it requires more coals than does the Liége furnace, due in part to the cooling of the retorts. The Belgo-Cornwall furnace requires, on the other hand, more labour, but consumes fewer retorts than does the Cornwall furnace. It is somewhat inferior to the latter, but far superior to the old Liége furnace. A furnace with gas

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[1] *Berg. und Hutt. Ztg.*, 1878, p. 387.

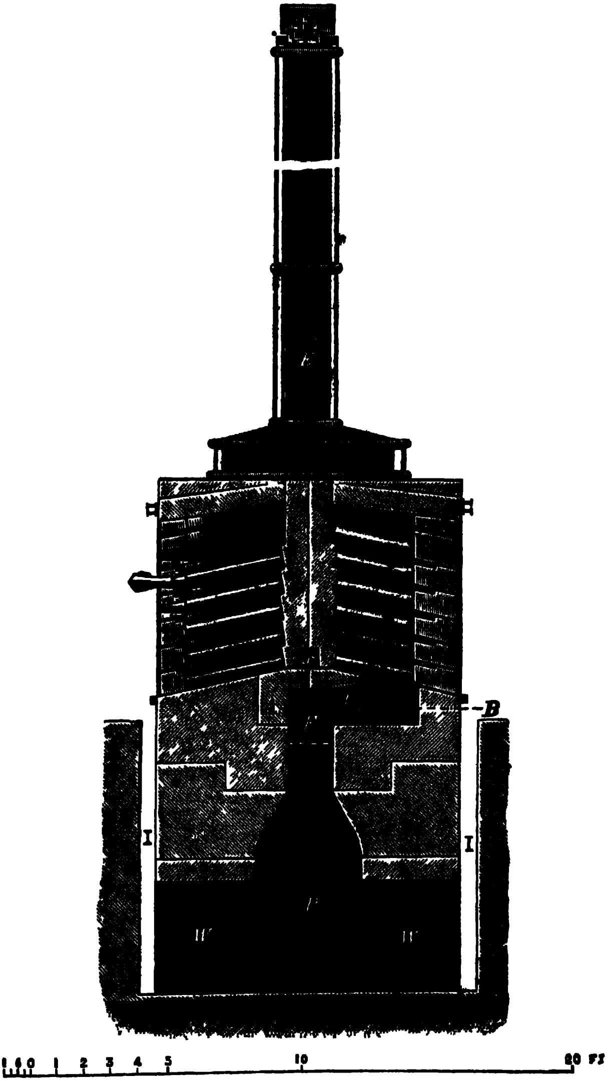

Fig 70

firing, on the Siemens principle, has been patented by the Actiengesellschaft für Glas-industrie, formerly Frederick Siemens', of Dresden.[1] It is not known whether this furnace has ever come into use.

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[1] D. R. Patent, No 50,917, September, 1889.

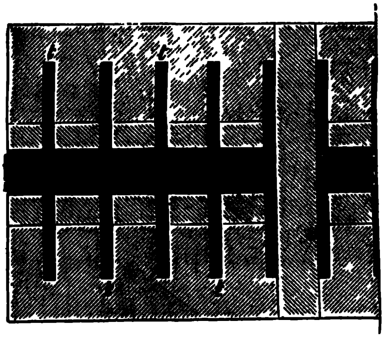

Fig 71

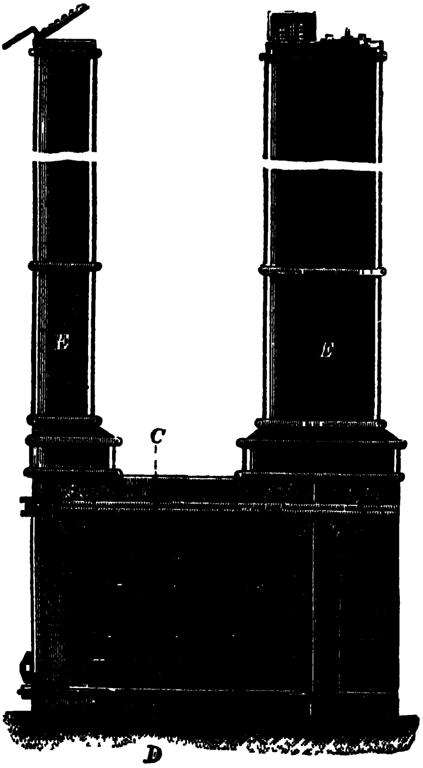

Fig. 72.

Double Furnaces

As an example of the double furnace with grate fire, the furnace which was in use in the year 1871 at the works of the Nouvelle Montagne, at Prayon, may be described. Its construction is shown in Figs. 70 to 72.[1] In these *V* is the vertical wall which divides the furnace into two parts. It also serves to support the rear ends of the retorts, the front ends of which are carried by slabs in the same way as in the single furnace. Each half contains 46 retorts in six tiers, the lower 5 rows consisting of 8 retorts each, whilst the upper one contains only 6. *F* is the fire-place with flat grate, the arch of which carries the above mentioned dividing wall. Above the arch there is an air flue for the purpose of cooling the brick work. On either side of the arch there are slots *t* at given distances apart, through which the flame enters both divisions of the furnace. In each division there are two flues *z*, in the arch of the furnace, through which the products of combustion pass into stacks *E*, 23 feet in height.

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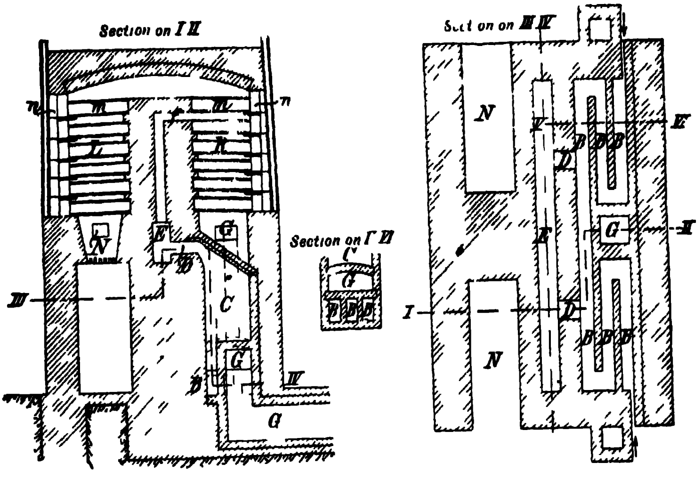
[1] Massart, *Rev. Univers. des Mines*, 1871, vol. xxix., p. 313; *Zeitschr. d. Ver. Deutsch. Ing.*, vol. xvi., pp. 10, 165.

The residues after distillation are discharged through the flue *I* into the vault *W*, and removed by means of the arched gallery *R* running beneath the grate.

2.—*Furnaces Fired by both Grates and Gas*

Hauzeur has designed a peculiar form of double furnace, fired both direct and by means of gas, which has been used with much advantage in Belgium and Spain.[1] The retorts of one division are heated by means of direct firing. The products of combustion, mixed with unburnt gases, escape at the upper end of this division and enter the second division, which they traverse from above downwards; in the second division the unburnt gases are completely burnt by the introduction of heated air. The construction of this furnace, which thus presents a combination of grate and gas-firing, is shown in Figs. 73 to 75,[2] *N* is the grate, upon which the fuel is only partly burnt by the introduction of a limited amount of air. The flame and unconsumed gas traverse the first division *L*, and then enter the second division *R*, in which the unburnt gases are completely burnt. The air required for this purpose enters the second division by means of flues *B*, *B*, in the walls of the furnace, passes out of these into the



FIGS 73–75

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[1] D. R. Patent, No 3,729, September 15, 1877.

[2] Spirek, *Oesterr. Ztschr*, 1881, p. 335; Dingler, 235, 221.

chamber *C*, thence passes through the horizontal flues *D* into the flue *E* in the central wall, escaping finally in a heated state through the horizontal apertures *f* into the upper part of the shaft *R*, where the unconsumed gases are completely burnt. The products of combustion descend in this shaft, escaping through the flue *G* into the stack. On their way they give off a considerable portion of their heat to the brick work surrounding the air flues.

3.—*Gas-fired Furnaces*

These furnaces are heated entirely by means of producer gas. They have the advantage, as compared with direct fired furnaces, of being independent of the nature of the fuel, of consuming less fuel and fewer retorts, and of extracting more zinc. The diminished consumption of retorts depends not only upon the uniform temperature *obtained by means of gas-firing, but also upon the existence of a slight plenum of pressure in the furnace, which prevents cold air from entering it*, whereas in a grate-fired furnace cold air enters the latter whenever fresh fuel is charged. In consequence of these conditions, the retorts are less apt to crack, and last longer. For the same reason the output of zinc is higher, because less zinc vapours escape from the retorts into the furnace. The air used for burning the gas should, as a rule, be heated. Gas furnaces with and without regenerators are employed. Furnaces with regenerators, although they consume less fuel and attain higher temperatures than the others, have been employed in but few cases, because their first cost is high, because the regenerator flues are easily choked by zinc oxide, and therefore require constant cleaning, because the temperature is not so easily kept at a uniform heat in the lofty Belgian furnaces as it is in the broad, but low Silesian furnaces, and because in consequence thereof the retorts are apt to be over-heated and zinc to be lost on account of the difficulty experienced in condensing the zinc vapours. In the case of the low and broad Silesian furnaces with large muffles, gasfiring with regenerators has given good results.

Gas-fired Furnaces without Regenerators

These furnaces have been used at Moresnet, in Belgium, and in the United States of North America. At Moresnet, generators with step grates as well as Grobe-Lürmann producers have been employed.[1] The latter form of producer has given results inferior to those obtained by the step grates. Two furnaces were united to form one block, but each furnace was provided with a separate producer. The two furnaces were not built directly back to back, but a flue into which the products of combustion escaped, separated them. The gases entered the furnace from the producers, when they came into contact with hot air heated in the bottommost row of the retorts, and were thus burnt. They ascended in the furnace and escaped from the upper end thereof into the above-mentioned vertical flue, through which they made their way downwards towards the stack. The furnaces used in the neighbourhood of Liége[1] are broader than they are high. They are built in pairs back to back, each separate furnace being provided with two gas-producers. The air is heated and is caused to enter the furnace at various places in order to heat the latter as uniformly as possible. Loiseau[2] passes producer-gas through a series of chambers leading one into the other and filled with retorts. Into the first heating chamber he admits cold air, into the following ones hot air, the temperature of which is gradually raised in proportion as the amount of combustible gases in the current diminishes. The object of this arrangement is to attain as uniform a temperature as possible in all portions of the furnace, so that loss of zinc, due to alternations of temperature, may be avoided.

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[1] *Allgem. Huttenkunde*, p. 213; *Wochenschr. d. Ver. Deutsch. Ing.*, 1877, p. 14.

The construction of the older type of gas-fired furnace at the Matthiesen-Hegeler Zinc Works, at La Salle, is shown in Figs. 76 and 77. The furnaces are double furnaces into which the gases enter from above. The topmost tier contains 36 retorts. These are 4 feet 3 inches long, 20 inches high, and 8 inches broad in the clear; below these there are four tiers of 42 retorts each, the length and diameter of which decrease from above downwards. Each side of the double furnace accordingly contains 168 retorts, not counting those in the topmost tier. The gases are generated in producers provided with step grates, not shown in the illustration. Passing into the horizontal flues *b*, they enter the vertical flues *c*, on either side of the furnace, and escape through the upper end of the latter through the slots *d* into the upper portion of the furnace. They are here burnt by means of a blast of air which enters the furnace through the blast main *G*, *g* by the tubes *f* and the slots *e*. The flame thus produced traverses the furnace from above downwards. The products of combustion escape through *i* into the flues *k*, *l*, to the stack. A portion of the heat of these gases penetrates through the walls of the flue *b*, and thus warms the gases entering the furnace.

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[1] *Wochenschr. d. Ver. Deutsch. Ing.*, No. 44.

[2] *Berg. und Hutt. Ztg.*, 1879, p. 171.

The modern furnaces at the above-named works[1] consist of a row of heating chambers communicating with each other, which are traversed in turn by the stream of gas, and are furnished with apertures for the introduction of hot air Each pair of furnaces have a back wall in common, and are united to form a block. There are 4 to 6 tiers of retorts in each furnace, each row consisting of 56 to 72 retorts. The largest block of two furnaces contains 876 retorts.

A gas-fired furnace has been designed by Thum for the treatment in retorts of zinc ores rich in lead, which does not, however, seem to have proved satisfactory in practice The retorts of these furnaces, shown in Fig. 78, lie at a steep angle and are open at both ends[2] They are charged from below and closed at their bottom end by a clay plug. The lead collects in the bottom portions of the tubes *C*, whilst the zinc vapours escape at the upper ends and are there condensed by means of suitable adapters. The gases generated in the producers enter the furnace through the flue *V* by means of a slot *y*, and here mix with air entering through the slots *x*, the products of

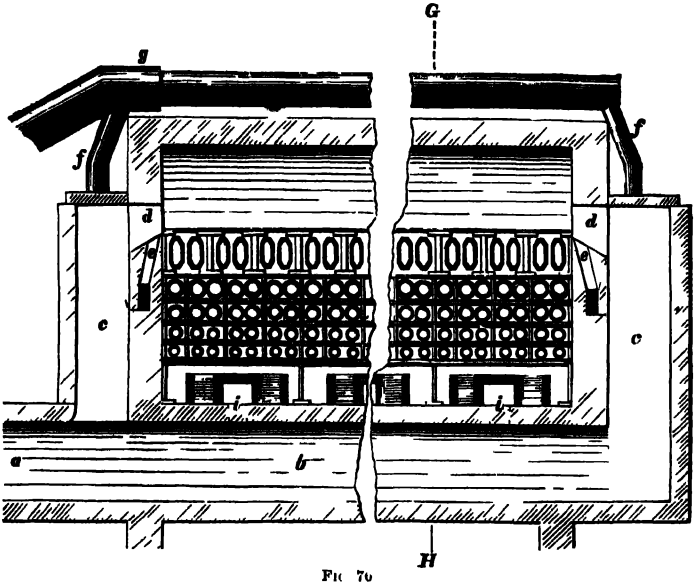

Fig 76

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[1] D R Patent, No 10,009, October 19, 1879

[2] Stolzel, *Metallurgie*, p 799, *Berg und Hutt Ztg*, 1875, p 1

combustion escape through the flue *z* into the flue *t*, whilst the air entering through the flues *r* is heated by the gases escaping through the former

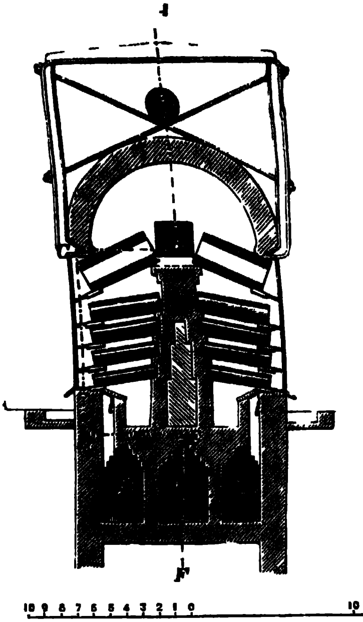

Fig. 77

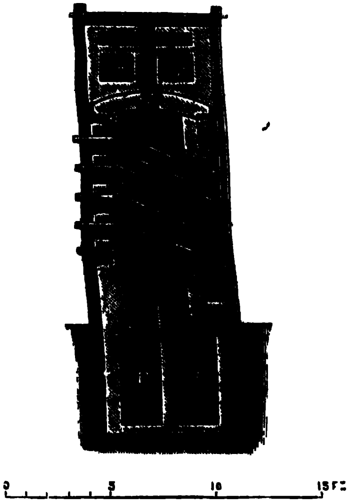

Fig. 78

Gas-fired Furnaces with Regenerators

The only furnaces of this kind that have up to the present come into use are furnaces on the Siemens principle. On account of the comparatively small diameter of the retorts, these furnaces produce higher temperatures than are required for the distillation of zinc, and have therefore only come into use in exceptional instances. The construction of a Belgian furnace on the Siemens principle is shown in Figs. 79 and 80. The furnace is double; *r*, *r* are the retorts, *W*, *W* the regenerators. The external pair of regenerators are gas regenerators, the inner ones air regenerators. The gas and air mix in the chambers *P*, the burning gases ascend one shaft, descend through the other, and traverse the regenerators lying below the latter on their way to the stack. After a certain interval—about half an hour—the direction of the air and gas currents is reversed.

The burning gases then ascend in the second shaft and descend in the first, escaping to the stack through the second pair of regenerators The gas current is reversed by the valve w (Fig. 80), which alternately connects the entering gases with one of the gas flues x and the products of combustion with the flue leading to the stack. A similar reversing valve, not shown in the figure, serves to reverse the air current as required. Such a furnace with 120 retorts on either side, 10 tiers of which are charged and 1 blank, is in use at the works of the Illinois Zinc Company at Peru, near La Salle.

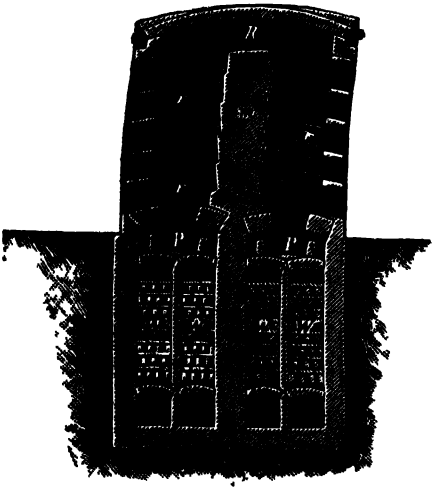

Fig. 79

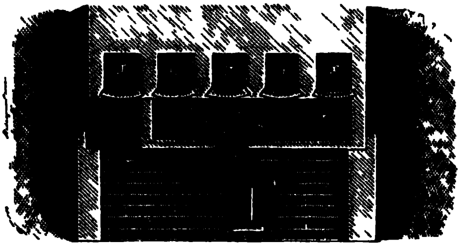

Fig. 80

Mixing the Charge

As already stated the ores, when various kinds are on hand, are so combined that the impurities thereof unite to form compounds which shall neither melt nor form fusible compounds with the material of the retorts at the temperature of distillation, whilst a moderately high output of metal shall result. Silicate of zinc needs no additions, because when finely ground it is reducible by coal alone. Blende, silicate of zinc, and zinc-bearing residues are charged in the form of fine powder; calamine, on the other hand, which is easily reducible, in coarser grains. According to their zinc contents, these ores are mixed with from 40 to 60 per cent. of their weight of lean coals, or small coke, or a mixture of equal portions of coal and coke. Gassy coal should be avoided, because some heat is absorbed in driving off the gas, and because the gases evolved dilute the zinc vapours, and thus make the condensation of zinc more difficult. Blende being more difficultly reducible than calamine, requires a larger admixture of coal. The ground materials are either mixed in troughs, or else in pug mills, or by means of rollers, in which last case, as in North America, the mixture is crushed a second time. The charge is slightly moistened to prevent its being blown out from the retorts by the gases evolved at the commencement of distillation. Binon and Grandfils prefer to mix the charge with tar and press it into blocks before introducing it into the retorts.

The Process of Distillation

When a furnace is to be started, it is gently fired for some days with empty retorts; afterwards the retorts are charged, and the heat gradually increased. The first charges are light, and are gradually increased, until at the end of 14 days the normal rate of working has been attained. The charges are introduced into the retorts, after the adapters have been removed, by means of a scoop shaped like a semi-cylinder attached to the end of a long rod. The retorts which are exposed to the greatest heat receive heavier charges than those less strongly heated. The latter are charged with easibly reducible substances such as zinc fume and zinc-bearing residues, as also with poor ores that sinter readily. In modern furnaces the average charge of a retort amounts to 63 lbs. of ore. After the retorts have been charged, the adapters with their supports are attached and the space between the adapter and retort is luted with clay. Some time after the retorts have been charged, a flame of burning carbon monoxide escapes from the adapters, which shows after some time the brilliant light of burning zinc vapours. As soon as this phenomenon is perceived, nozzles are attached to the adapters in order to avoid loss of zinc. Although the adapters rapidly attain the necessary temperature, no fluid zinc condenses in them at first, zinc oxide being formed in consequence of the carbon dioxide and water vapour present in the gases. Moreover, on account of their great dilution the vapours of zinc do not condense to a liquid, but form fume. It is only after the above-named gases have disappeared that the zinc vapours begin to condense to liquid zinc. If the furnace works too hot, whereby the formation of considerable quantities of zinc fume in the nozzles is caused, due to imperfect condensation of vapours in the adapters, a few small holes are made in the clay luting. The zinc condensed in the adapters is removed either several times during the process, or only once after its completion. In this case the nozzles are removed from the adapters and the zinc is drawn by means of a rake out of the adapters into ladles held beneath them, from which it is cast in iron moulds into slabs weighing 40 to 44 lbs., the surface of the zinc being first skimmed. The time of distillation depends upon the size of the retorts and of the furnaces, upon the position of the retorts in the latter, and also upon the reducibility of the charge, and averages between 12 and 24 hours. After its conclusion, the adapters are removed and the residues remaining in the retorts are drawn out by means of suitable rakes. After any accretions have been removed, the retorts are charged again. Damaged retorts are changed after the conclusion of the distillation. The time occupied in charging, clearing the retorts, repairing the latter, and replacing damaged retorts, depends upon the size of the furnace and the number of retorts it contains.

The same conditions control the number of men required at the furnace. For modern Belgian furnaces, the retorts of which contain on an average 63 lbs. of ore, one man is reckoned to every 14 retorts per 24 hours. The extraction of 1 ton of zinc from ores containing 50 per cent. of metal requires 5·8 men per 24 hours. The charge of a furnace depends upon the number of retorts in it, and varies between 8 cwts. and several tons of ore. The consumption of fuel varies with the quality of the coal and the method of firing, between 1¼ and 2 tons for each ton of ore. The durability of the retorts depends upon the quality of the materials employed and upon the method of manufacture. Modern retorts made by hydraulic pressure last at present upon an average 40 days. The loss of zinc, which was formerly up to 27 per cent. of the contents of the ore, varies with modern furnaces between 10 and 15 per cent.

Examples of Zinc Extraction in Retort Furnaces

The commercial results attained with modern furnaces fired by gas are far more favourable than in the case of the older furnaces. For the production of 1 ton of zinc from ores containing 50 per cent. of metal, 3 to 4 tons of coal for heating and reduction, and 4 cwts. of clay are required, 2·5 per cent. of the retorts being destroyed daily. With the oldest furnaces 7 to 8 tons of coals were consumed for each ton of zinc.

The double furnaces at the works of the Vieille Montagne Company at Angleur, contain 100 retorts on either side, a block of furnaces containing 400 retorts. They are fired by means of gas and hot air. Each retort receives a charge of 66 lbs. of ore and 26·5 lbs. of coal, and produces in 24 hours from 26 to 33 lbs. of zinc, together with a certain quantity of zinc fume. For the extraction of 1 ton of zinc 3·5 to 4·5 tons of coal are consumed for fuel and reduction. The loss of metal amounts to 15 per cent.; the retorts last from a fortnight to four months, according to their position in the furnace and the care used in their manufacture. A furnace lasts two to three years.[1]

Of the older types of furnace, the Liége furnace with 70 retorts fired by means of a grate, and the grate-fired double furnaces with 92 retorts of the Nouvelle Montagne, at Prayon, may be mentioned, the results quoted having been obtained in the seventies. The Liége furnace was 5 feet deep, 8 feet 6 inches broad, and 9 feet 10 inches high, and contained 70 retorts each 3 feet 3 inches long, with 9½ inches outside, and 7½ inches inside diameter, and treated in 24 hours 26 cwts. of charge with a consumption of 14 cwts. of coal for reduction and 2 tons of coal for fuel, the ores containing 47 to 48 per cent. of zinc. The output of a furnace per 24 hours amounted to 9¼ to 9½ cwts. of zinc; the loss of zinc, including that left in the residues, amounted to 18 per cent. Residues containing more than 6 per cent. of zinc were concentrated by dressing, and then treated either in the upper retorts of a Belgian furnace for the extraction of zinc, or in a reverberatory furnace for the production of zinc white. The already described double furnace of the Nouvelle Montagne Company, at Prayon,[2] with 92 retorts, was charged with 8 cwts. of ore (calamine and blende) containing 40·32 per cent. of zinc, 160 lbs. of rich residues from the zinc works, such as zinc fume and skimmings, and 366 lbs. of coal for the reduction, during the day shift. On the night shift the furnace worked hotter and was charged with 10 cwts. of ore. The charge was distributed as follows:—

	lbs. of Ore.	lbs. of Coal	lbs. of Residues.
Retorts of the bottom tier	24¼	6½	
Retorts of the third tier	37½	6	
Retorts of the fourth tier . . .	16¼	8	6½
Retorts of the sixth tier	11	11	11

Charging the retorts occupied 3¼ hours. The residues left after distillation in the upper retorts contained on an average 9·15 per cent. of zinc, those in the middle tiers 4·67 per cent. of zinc, and those in the lower tiers 2·28 per cent. The loss of zinc amounted to 11·28 per cent. The retorts in the topmost row lasted for 90 days, those in the bottom row only for 6 days. The furnace campaign lasted 150 to 180 days. As will be seen, these older retort furnaces fired by means of grates, were markedly inferior to the modern furnace both as regards their durability and capacity, and have been to a great extent replaced by the latter. The larger furnaces, fired by gas, should therefore be preferred as a rule to the smaller grate-fired furnaces.

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[1] *Bull. de la Soc. de l'Industrie Min.*, 1888, p. 505.

[2] Massart, *loc. cit.*

The zinc works in the Eastern States of North America (Bergen Port, Passaic Works, Newark and Bethlehem) employ Belgian furnaces with Wetherill grates burning anthracite.[1] The following is an account of the process as practised there towards the end of the seventies. At the Bergen Port Zinc Works, New Jersey, where calcined blende containing 26 per cent. of oxide of iron was treated, the furnace contained 70 retorts. Each furnace could put through 3,175 pounds of calcined blende with 1,900 pounds of anthracite for reduction, in 24 hours, with a consumption of 2½ tons of anthracite for fuel. The loss of zinc varied from 24 to 26 per cent. The two topmost tiers of retorts were only charged once in 24 hours, the five lower tiers twice. The condensed zinc was removed six times in 24 hours from the adapters. The consumption of coal per ton of zinc amounted to 5·5 tons for heating and 1·9 for reduction, or altogether 7·4 tons. Every 24 hours five retorts were destroyed per furnace, or 7·1 per cent. The reason of the comparatively great consumption of fuel and of retorts, together with the high loss of zinc, was caused by the large percentage of iron in the charge. The furnace campaigns lasted about a year.

At the Passaic Zinc Works, in Jersey City, the furnaces also contain 70 retorts each. The charge for the furnace consists of 27 cwts. of a mixture of willemite and calamine. The three lower rows are charged twice in 24 hours, the remaining ones only once. In 24 hours 10 cwts. of zinc are produced, with a consumption of 2¼ tons of coal for fuel. The extraction of zinc amounts to 80 per cent. of the contents of the ore. One ton of zinc requires 4·5 tons of coal for fuel and 1·3 tons for reduction, or a total of 5·8 tons. In 24 hours 6·4 per cent. of the number of retorts in the furnace was destroyed. A furnace campaign lasts two years.

At the Lehigh Zinc Works, near Bethlehem, Pennsylvania, the furnaces contain 56 retorts, and hold a charge of one ton of ore, consisting of a mixture of calamine and blende. The topmost row of retorts, containing zinc fume and skimmings, is only charged once in 24 hours, the six lower rows twice. For one ton of ore 1·8 tons of coal are consumed as fuel. The production of zinc amounts to 73·5 per cent. For each ton of zinc 4·5 tons of coal as fuel and 1·7 tons of coal for reduction, or a total of 6·2 tons of coal are required; 3·7 per cent. of retorts are destroyed daily. The furnace campaigns last for 15 months.[1]

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[1] Strecker, *Jahrb. d. K. K. Bergak.*, 1879, p. 282.

At the Bertha Works, near Pulaski in the State of Virginia,[2] which produce zinc well known for its purity and freedom from lead (Zn 99·981 per cent., Fe 0·019 per cent.), the ore treated being calamine free from lead, there are 10 modified Belgian furnaces fired by grates, each of which contains 140 retorts, of oval cross-section, having a length of 4 feet, the larger diameter being 10 inches and the smaller being 8 inches in the clear. Long-flamed Pocahontas coal is used as fuel, anthracitic coal for the purpose of reduction. The charge of a furnace consists of 4·25 tons of calcined ore and 3 tons of coal. The distillation occupies 24 hours, the output of zinc being 80 per cent. Five men work a furnace in 24-hour shifts.

At the works of the Matthiesen and Hegeler Manufacturing Company at La Salle,[3] there were towards the end of the seventies two forms of gas-fired furnaces, namely, small double furnaces with 136 retorts, and a large double furnace with 408 retorts. The producers were provided with oblique grates built of fire-brick. The bricks were supported upon cast-iron bearers, the necessary space for the admission of air being left between them. This arrangement is necessitated by the fact that the only available coal is very apt to clinker. There were five tiers of retorts in all the furnaces. The uppermost row consisted of the retorts with rectangular cross-section described on page 105, which take a charge two or three times as great as that of the regular retorts. The furnaces were divided into sections, which contain 4 tiers of 7 cylindrical retorts, and 1 row of 6 prismatic retorts each. The smaller furnaces have two of these divisions on either side, the larger six; the topmost row against which the flame strikes was first charged with blende, the second and third with calamine, and the lowest with zinc fume and residues rich in zinc. The output of the large double furnaces amounts to 5 to 6 tons of zinc per 24 hours. The loss of zinc is 18 per cent.; the destruction of retorts amounts to 25 per cent. At present the largest double furnace contains 876 retorts.

The gas-fired furnaces of the Missouri Zinc Company, in St. Louis,[4] contain 160 retorts each. They are charged with calcined silicate of zinc, the weight of which in the raw state amounts to

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[1] Strecker, *loc. cit.*

[2] *Eng. and Min. Journ.*, 1893, vol. lvi., No. 22.

[3] Strecker, *loc. cit.*

[4] Strecker, *loc. cit.*

4½ tons. The amount of coal employed for the reduction of this charge is 31·5 cwt., 8 tons of coal being consumed as fuel. The output of zinc is equal to 70·71 per cent. For each ton of zinc 4·4 tons of coal are used as fuel. The destruction of retorts is considerably less than it is in direct-fired furnaces.

II.—Zinc Distillation in Muffles, or the Silesian Process

This form of distillation, as already stated, is carried out in reverberatory furnaces in which muffles are arranged. The gaseous zinc thus produced is condensed in adapters of various forms attached to the muffles.

Muffles

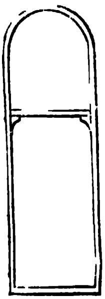

Fig. 81.

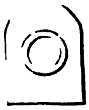

Fig. 82.

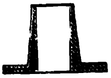

Fig. 83.

The muffles, as previously stated, generally assume the shape of prismatic boxes, with an arched top. In some instances they consist of oblong boxes flat on top, with rounded edges. The rear side is closed whilst the front remains open. During the distillation the lower half of the latter is closed by means of a fireclay slab, whilst the upper portion is closed by the end of the adapter, which is luted on tightly with clay. The front end of the adapter rests upon a step supported on either side by projections from the longer walls of the muffle. If the front end of the adapter is tube-shaped, the upper half of the muffle must be closed by means of a slab of clay, provided with a short cylinder into which the end of the adapter fits. The front end of the muffle and the upper plate with its short cylinder are shown in Figs. 81 to 83. As has been stated above, the muffles are generally 26 inches high in the clear, 6 to 8 inches wide, and 28 inches to 7 feet long. If the entire bottom of the muffle is supported, its length may be as much as 7 feet. If, however, it is only supported at the front and back ends, its length must not exceed 4 feet. The bottom and sides of the larger muffles are made thicker at the back than in front. In Upper Silesia, for instance,[1] the thickness of the walls increase from the front to the rear portion of the muffle from 0·8 to 1·2 inches in the arch, and the thickness of the bottom from 0·8 to 2·5 inches. The thickness of the smaller muffles made by hydraulic machinery in the Rhine Provinces and Westphalia only averages about 1 inch. Long muffles, up to 5 feet 6 inches in length, are exceptionally made with a bottom as much as 2 inches thick, in order to render them more durable, as, for example, at Birkengang, near Stolberg. The material from which the muffles are manufactured is a mixture of raw and burnt clay, the latter of which may be replaced in part by fragments of muffles. The composition of suitable varieties of clay has already been given on page 91. The proportion in which the various constituents are mixed depends upon the proportion of silica and alumina contained in the material available. For example, at the Hamborn Works 60 parts of burnt Belgian clay, 35 parts of raw Belgian clay and 5 parts of coke are used. At the Birkengang Works two-thirds of burnt and one-third of raw Belgian clay; at the Munsterbusch Works, near Stolberg, 60 per cent. of burnt and 40 per cent. of raw clay, together with coke dust; at the Freiberg Works 1 part of raw and 2 parts of burnt clay; at the works near Dortmund 2 parts of burnt, 1 part of raw clay, and one-tenth of finely ground coke; at the Upper Silesian Works 55 to 65 per cent. of burnt clay and 35 to 45 per cent. of raw clay. The fireclay used in Upper Silesia is obtained from Saarau, in Upper Silesia, from Briesen in Moravia, and from Szczakowa in Galicia. A clay shale from Neurode is also used. The crushing, mixing, and kneading of the above-named materials is performed in the same way as in the manufacture of retorts for the Belgian furnaces. Burnt clay must be crushed down to a size not exceeding 0·3 to 0·4 inch.

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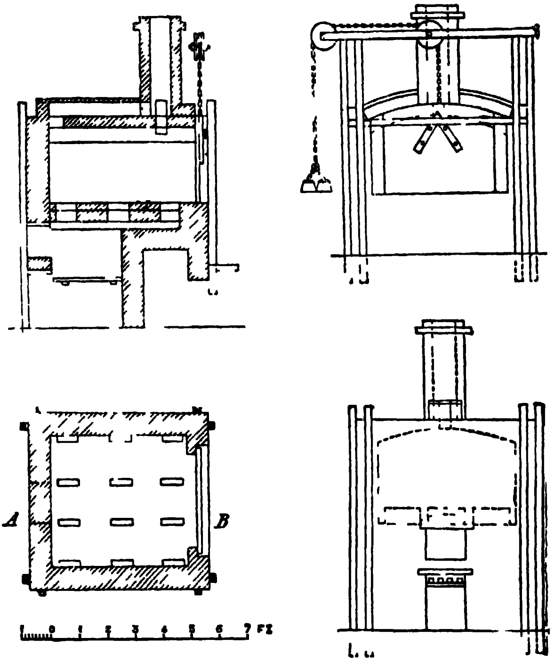
[1] Georgi, *Berg. und Hutt. Ztg.*, 1877, p. 72.

Muffles are manufactured either by hand or by means of machinery. In Upper Silesia, where only big muffles are employed, these are made by hand. In Belgium, the Rhine Provinces, and Westphalia, on the other hand, where small muffles only are in use, machinery is used for their manufacture. When made by hand, muffles are made either vertically or horizontally. When vertical muffle moulds are employed, the latter generally consist of three sections fastened together by means of hooks and eye bolts. As in the manufacture of retorts, the back portion of the muffle is first shaped in the bottom portion of the mould, the second section is then attached to the first and the middle of the muffle is shaped in it, and then the front section is attached to the former portion, and the rest of the muffle moulded in it. Finally, the projections to carry the step at the front portion of the muffle are attached. The various slabs of clay are fastened to each other as in the case of the retorts, by scoring the portions in contact by means of a small comb. When the muffles are made horizontally, as in Upper Silesia,[1] the bottom is first made by cutting out a hollow in a prismatic piece of clay of the size of the bottom of the muffle, which is then placed in the lower portion of the muffle mould. Slabs of clay of the height of a segment of the mould are then introduced and united, the diagonally cut end of the slab being scored, moistened with water, and then pressed against the correspondingly cut end of the next piece The slabs of clay are then pressed against the corresponding portion of the mould and beaten down with an iron beater. This process is continued until the muffle is complete. Generally four or five muffles are commenced simultaneously; the advantage obtained thereby is that when the work is completed the muffle is already dry enough to admit of the mould being removed.



Figs 64—67

In Belgium, the Rhine Provinces and Westphalia, muffles are made by hydraulic machinery in the same way as the retorts for the Belgian furnaces, the muffles being dried standing on end for a certain time, up to one month, in drying chambers heated to between 30° and 33° C., then glazed if desired, and finally kept until required for use (up to a period of 12 months) in drying chambers at a temperature of 35° C.

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[1] Georgi, *loc. cit.*

Muffles must be introduced red-hot into the furnace. They are therefore previously heated by the waste heat of the distillation furnace, or in special reverberatory kilns provided with grate fires. The construction of such a furnace is shown in Figs. 84 to 87. Above the grate there is an arch pierced with twelve openings, through which the flame enters the heating chamber; the latter is provided with a door lined with firebrick, which can be raised or lowered by means of counterpoises. At the Paul Works, near Rosdzin, in Upper Silesia, such a furnace takes 12 to 14 muffles at a time. Their heating or annealing lasts 12 hours, 5 cwts. of coals being consumed. A muffle lasts 30 to 40 days.

Condensers or Adapters

These are of various shapes. In the older Silesian furnaces they consisted of a bent clay pipe composed of several pieces which communicated with a chamber in which the zinc, condensed in the pipe, accumulated. In the newer furnaces they are given the form of cylindrical tubes, or of cylindrical tubes bellied below, or of prismatic boxes with an arched top. The arrangement of the adapter for the old Silesian furnace, which is now no longer employed, is shown in Figs. 88 and 89. In the former, *h* is the chamber in which the fluid zinc solidifies; in the latter figure *a* is the upper portion of the adapter

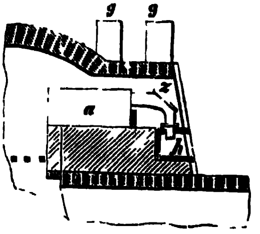


FIG. 88.

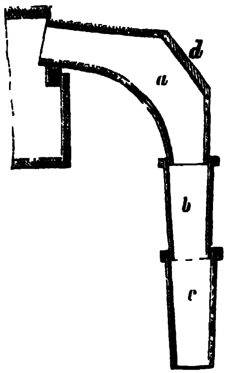
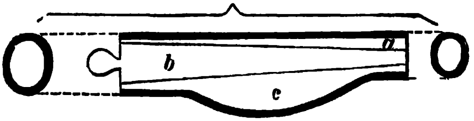


FIG. 89.

made of clay, which rests upon the step of the muffle. It has an aperture at *d* which can be closed by a tile; the muffle can be charged through this aperture by removing the latter; *b* is a tube made of cast-iron, *c* one of sheet-iron, the latter entering into the collecting chamber. The zinc condenses in the knee-shaped tube, and flows through the vertical portion into the chamber. The employment of this adapter makes it necessary to re-melt the solidified zinc, in order to cast it into moulds. As above mentioned, it has been replaced by other forms of adapters. Adapters which have the shape of tubes bellied underneath are shown in Figs. 90 and 91. The fluid zinc collects in the bellied portion and is raked out from it from time to time; a sheet-iron cone or nozzle is attached to its front end. Inclined cylindrical tubes, as shown in Fig. 92, are also used as adapters. In this case their front end is closed with a tile, or with an iron plate clayed over, and having a hole through the centre. The zinc that collects in this adapter is allowed to run into an iron ladle held in front of it, by removing or loosening the plate; for this purpose the clay luting which connects the lower portion of the plate to the adapter is gradually loosened. The same method of closing is used for adapters made in the shape of prismatic boxes. The gases escape through a short tube projecting from the front slab into a nozzle. In order to condense the zinc vapours more completely, to collect zinc fume, and to avoid the injurious effects of the gases and vapours escaping from the adapters, these have received important improvements in recent times in Upper Silesia. Of these new adapters, the most important are those of Kleemann and of Dagner.



FIGS 90 and 91

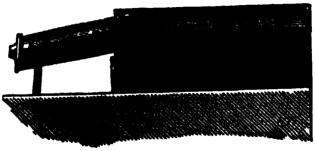


FIG 92

The Kleemann adapter is shown in Fig. 93,[1] and has the shape of an inclined cylinder, or of a parallelopipedon, or of a prismatic box with arched roof 3 feet 3 inches long, to the front portion of the roof of which a flange 4 inches high is attached. Above this is a cast-iron grating upon which a layer of coke is maintained at a red heat. The back portion of the adapter is secured to the muffle; the front, open portion is closed with an iron plate covered with clay and luted as tightly as possible to the adapter. There is an opening in the centre of the plate, which can be kept closed by means of a clay plug. The whole adapter lies inside the recess of the furnace. The gases, consisting mainly of carbon monoxide and of the metallic particles which are not deposited in the receiver, are forced to pass through the grating and the layer of glowing coal. A portion of the metallic constituents of the vapour is retained in the layer of coke, whilst the carbonic oxide is heated to the point of combustion, and is burnt by a current of air. Any zinc oxide contained in the gases is not reduced by the bed of coke. As the layer of coke soon becomes stopped up, it requires frequent stirring, and must be renewed from time to time. In consequence of the layer of glowing fuel upon the grate, no oxygen from the air can enter the adapter. The burnt gases and the metallic particles not retained in the bed of coke pass through an opening in the arch of the recess into a flue running above the furnace, or into a main flue, whence they are conducted into an apparatus for the precipitation of the metallic particles, and finally escape into the stack. In the above figures the burnt gases escape from the adapter *v*, through the grating at *a*, by the opening *o* and the flues *b* and *c*, into the main flue *D*, and from the latter into the stack. The zinc is tapped out from the bottom end of the adapter. These adapters are at present in use at the Silesian Works, near Lipine. The gases and vapours escape through the layer of burning fuel into a main longitudinal flue, thence into an underground dust chamber, and finally to the stack. No deposit of oxides may show upon the coping of the stack, as this would be a sign that the flue dust has not been completely collected. There is a small sight-hole at the front of the adapter, which can be kept closed by clay. If any flame escapes from this sight-hole, it shows that the passage of the vapours through the layer of fuel has been hindered by the deposition of particles of metal and oxides in the latter, which obstacles must then be removed or the bed of fuel

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[1] D. R. Patents, Nos. 8,121, 12,821, 28,596; additional Patent, 7,411.

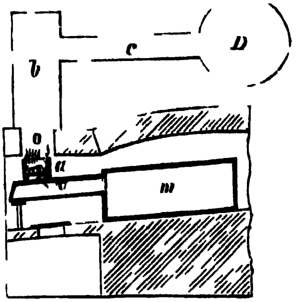
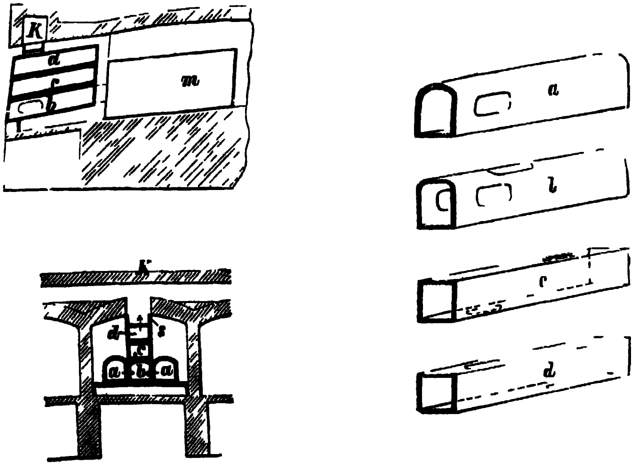


FIG 93

be renewed. This adapter, which has rendered good service at the Silesian Works, has been replaced in other works in Upper Silesia, such as the Wilhelmina and Paul Works, by the Dagner adapter.

The Dagner adapter[1] serves to condense the zinc vapours from a pair of adjacent muffles, and consists of a series of inclined boxes which lie beside or above each other, in which the greater portion of the metallic constituents of the vapour is deposited. The arrangement of the adapter is shown in Figs. 94 to 99; in these *a*, *a* are the two adapters fitted to the pair of muffles *m*, lying side by side The gases and zinc vapours escape from lateral openings in these adapters into a chamber *b* lying between them. Through an opening in the upper part of the latter they escape into a prismatic box *c*, 24 inches long, traverse this lengthways and then rise up into another prismatic box *d* of the same length, which they also traverse longitudinally, and then escape through an opening provided with a short branch into the flue *K*. When they escape through the topmost box, these gases are burnt by a current of air, so that their products of combustion, together with any zinc vapours that have escaped combustion, enter the flue *K*. The front ends of these adapters are closed by plates of sheet iron, which are covered with clay on either side, and are luted to the adapters. In the middle of each plate there is a small round hole, which can be closed at will by a clay plug. Through these



Figs 94—99

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[1] D. R. Patent, No. 6,958.

holes iron rods can be introduced into each separate portion of the adapters in order to remove deposits of zinc oxide from within them. The separate recesses are closed in front by plates of sheet-iron.

The zinc collects in the lower adapter in the fluid condition; in the upper adapters zinc oxide and zinc fume are deposited. The zinc is tapped off from the front end of the adapters. From the other adapters the zinc fume and oxide are raked out after the front plates have been removed. On account of the long distance which the gases have to traverse through these adapters and boxes, the greater portion of their metallic constituents is deposited. The remainder, together with any zinc oxide formed by the combustion of zinc vapours at the outlet, passes into dust chambers connected with the adapters. The division *b* of the adapter is 6 inches broad, and 8 inches high; the division *c* is 4¾ inches broad and 4 inches high; the division *d* is 10 inches broad, and 10 inches high. The burnt gases and vapours after passing through the main flues, dust chambers, and dust towers, finally pass into a flue with a powerful draught. At the Paul and Wilhelmina Works, near Schoppinitz, the gases escape through horizontal pipes. The recess is here closed in front by a temporary wall, in the lower portion of which there is a small opening. Through the latter the air required for burning the gases enters the recess and directs the flame towards the collecting flues. Through these flues the gases pass into a system of condensing chambers. These chambers of which there are 7, having a total length of 360 feet, are provided with vertical walls, by which the distance to be traversed by the current is prolonged and the surface exposed to it increased. In the last chamber any remaining solid particles, carried by the current of gas, are removed by means of a water spray, after which the gases escape into the stack. The water flowing through this last chamber is run on to a coke filter, which retains the solid particles, the water running clear from the last filter. This arrangement has given satisfactory results. The composition of the zinc fume collected in the condensing chambers of the Wilhelmina Works when the Dagner adapter is used, is the following:—

ZnO	88·20	per cent.
CdO	1·46	„
PbO	4·44	„
SO_3	4·12	„
Mn_3O_4	0·05	„
Fe_2O_3 and residue	1·50	„
	99·77	

Adapters are composed of ordinary potter's clay with the addition of a certain quantity of burnt clay or of fragments of muffles, or at times of the distillation residues from the zinc retorts, or of coke dust. They are made by hand, slabs of clay of the requisite length being laid upon wooden cores of the shape of the adapter, and pressed down upon them. As soon as the mass has attained a sufficient degree of consistency, the core is withdrawn. When a bellied adapter has to be made, as is shown in Fig. 90, the core consists of three pieces, *a*, *b* and *c*, the middle wedge-shaped portion of which, *b*, is provided with a handle, so that it can be drawn out. The slab of clay is laid upon the core and beaten down by hand. As soon as it has attained a sufficient consistency, the wedge-shaped portion of the core is withdrawn; the portion *a* then drops down, and can be drawn out, and the portion *c* is lastly lifted out from the adapter. These adapters are either dried upon the roof of the distillation furnace and used raw, or else are burnt after having been dried by the waste heat of the distillation furnace, or in special annealing kilns. Adapters last from two to three weeks.

In order to protect the workmen against the gases and vapours which escape when the muffles are being cleared out and charged, as also against the zinc vapours which escape during distillation, through the sight-holes and through cracks in the adapters, an arrangement has been introduced by Stempelmann at the Hohenlohe Works, near Kattowitz, with good results. It is therefore combined with the Dagner adapter, the arrangement being shown in Figs. 100 to 102.[1] Above the uppermost adapter a sheet-iron plate *a b* is so secured to the buckstaves of the furnace as to form a flue, the walls of which consist of the above sheet-iron, the true furnace wall *c d*, and of a pair of buckstaves *s*. At the upper end there is a lateral aperture *i* through which the gases and vapours ascending can escape into the dust chamber *K*. This flue can be prolonged downwards by means of a sliding sheet of iron provided with a handle and suspended by means of a chain with a counterpoise. It is guided by means of iron castings *f* riveted to the sheet iron *a b*. When the muffle is to be cleared out, the sliding sheet is lowered so far that the gases and vapours escaping from the former rise through the opening *h* into the prolongation of the flue, and thence escape through the opening *i* into the dust chamber *K*. When the muffle is being charged, the sheet-iron must be lifted up so far that the front end of the adapter *V*, through which charging takes place, stands open. The gases and vapours then also escape

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[2] Saeger, *Hygiene der Hüttenarbeiter*, Jena, 1895.

into the above-named flue, and find their way through *i* into the dust chamber.

Wherever the adapters of Kleemann and Dagner are not in use, nozzles or condensers of sheet-iron are often attached to the front end of the adapters in order to collect the metallic portion of the vapours and to prevent injury by the escaping gases. The metallic portion of the vapours condense and thus form a mixture of pulverulent zinc and zinc oxide, known as zinc fume or "*poussière*." These

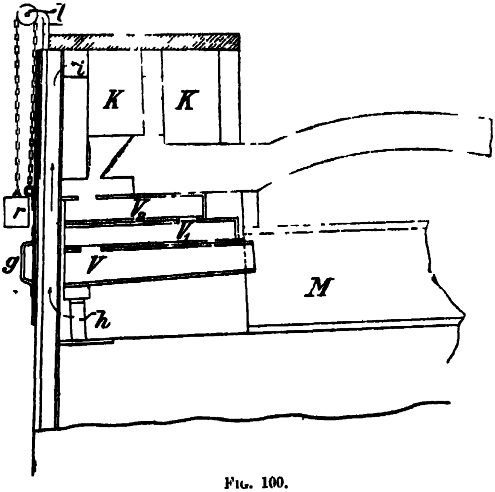

Fig. 100.

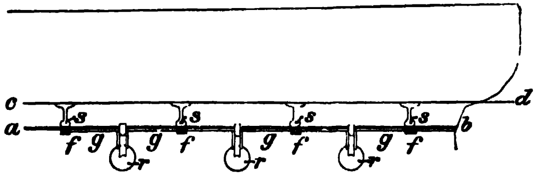

Fig. 101.

nozzles may communicate with draft flues to remove the poisonous carbonic oxide; otherwise this gas escapes through the front end of the former. Such nozzles are at present universally used for Belgian and Belgo-Silesian furnaces. The most improved forms of these, formerly used in Upper Silesia, and still at present used to some extent, are the twin cylindrical nozzles of Recha, the cylinder of Bugdoll, the vertical nozzle with condensing chamber, and the respective apparatus of Palm, of Hawel, of Mielchen and of Steger.

Fig. 103 shows Recha's nozzle. It consists of two cylinders of sheet-iron *A B*, connected with each other. The sight hole of the cylinder *A* is closed by an automatic valve *z*; the cylinder *B* has a cap *y*. The gases which are not combustible escape through the latter cylinder by means of the tube *x*, and can be conducted away by means of a hood attached to the front side of the furnace into the flues or above the level of the furnace top.[1]

Fig. 104 shows the nozzle of Bugdoll.[2] It consists of a cylinder closed in front; by means of a valve *b*, the particles of fume deposited in the cylinder can be removed. The gases and vapours escape through the branch *v*; the latter is closed by a gas filter of fine cotton in which all solid parts of the gases and vapours are retained.

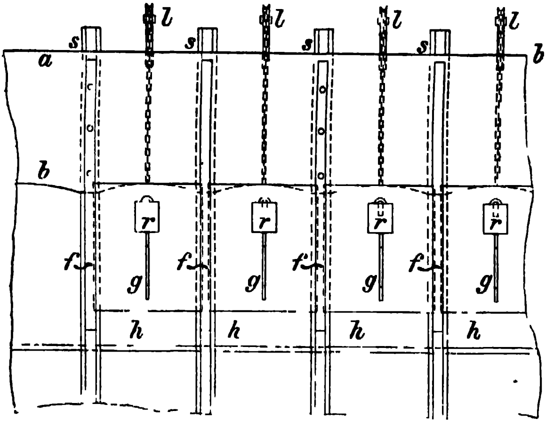

FIG. 102

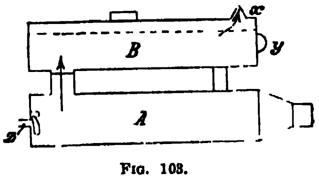

FIG. 103.

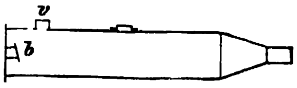

FIG. 104.

Fig. 105 shows the vertical nozzle with condensing chamber; *b* is the vertical nozzle connected on one side with the adapter *v*, by means of the tube *t*, on the other side with the condensing chamber *k* by means of the tube *s*. Through the latter, gases and vapours that have not been condensed escape by the tube *l* into the interior of the distillation furnace, where they are burnt. By means of two apertures provided with sliding covers the nozzle *b* can be cleared out.

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[1] D. R. Patent, No. 12,768.

[2] D. R. Patent, No. 11,545.

The apparatus of Palm[1] is shown in Fig. 106; the gases and vapours escaping through the adapter *v* pass through the tube system *r*, *r*, into the collecting tank *l*, filled with water, and in escaping impinge upon the surface of the water. From this tank they pass through several other washing tanks, and then escape into the fireplace of the furnace.

In Hawel's arrangement, shown in Fig. 107[2] a chamber *k* is provided over every pair of adapters, the former being connected with a gas delivery tube *n*. The nozzle is connected both with the chamber and with the gas tube by means of short pipes. The vapours pass first into the chamber, then into the nozzle, and finally into the gas flue. The greater portion of the zinc escaping through the adapter is condensed in the chamber *k*, and flows back into the adapter *z* over the inclined floor of the former. By means of a pipe recently placed by Hawel between the adapter and the chamber, better results have been obtained as regards the condensation of zinc vapours.

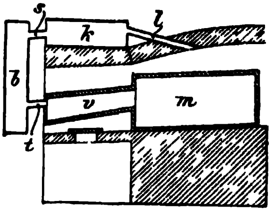

Fig. 105

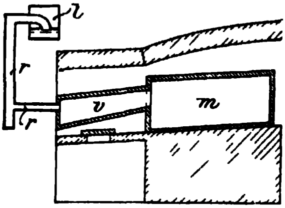

Fig. 106

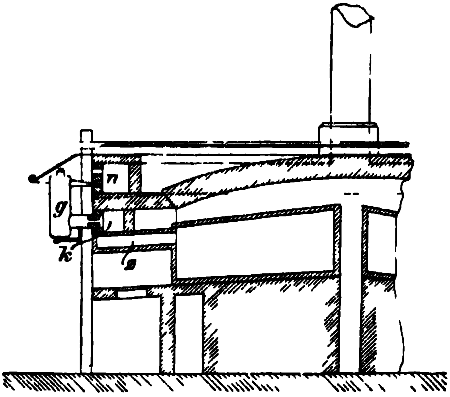

Fig. 107

The nozzle of Mielchen[3] used at the Hugo Works, in Upper Silesia, is shown in Figs. 108 to 110.[4] There are two adapters *d*

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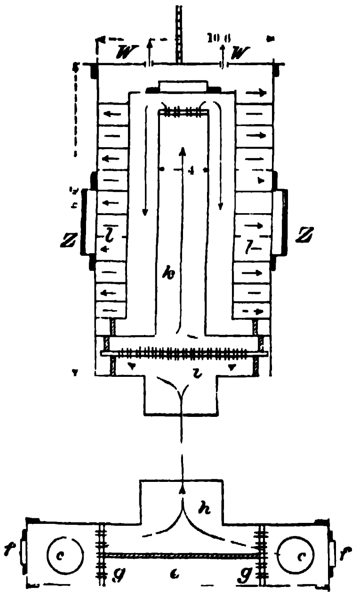
[1] D. R. Patent, No. 9,672.

[2] D. R. Patent, Nos. 57,385 and 61,740.

[3] D. R. Patent, No. 18,635

[4] Saeger, *op. cit.*

Fig. 110, from which the gases and vapours escape through two tubes of sheet-iron *c* into a sheet-iron cylinder *e*, provided with hand holes *f*, and pass by means of the perforated sheets *g* into the tube *h*, upon which the nozzle proper is supported. The latter consists of an inner cylinder of sheet iron *k*, resting upon a perforated iron plate *i*, the upper end being also perforated, and of an iron cylinder *l* which slips over the former, and which is in its turn surrounded with nine spiral rings made of sheet-iron, which are tightly riveted to the outer wall. The gases and vapours escape through the perforated cover of the inner cylinder into the annular aperture between the inner and the outer one, through the lower end of this space pass at the lower end of the latter into the space between the inner cylinder and the nozzle, and then take the spiral route indicated by the arrows, escaping finally through the openings *W* in the cover of the nozzle; the apparatus is provided with the handles *Z*. On account of the long route traversed around the outer cylinder, the deposition of the metallic portions of the gases is almost complete.



Figs 108 and 109

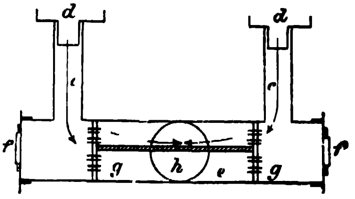


Fig 110

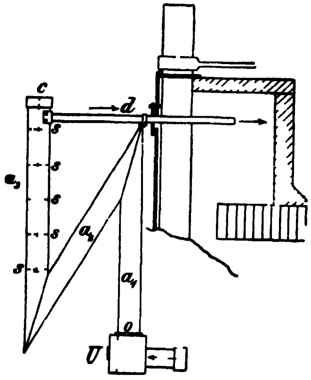
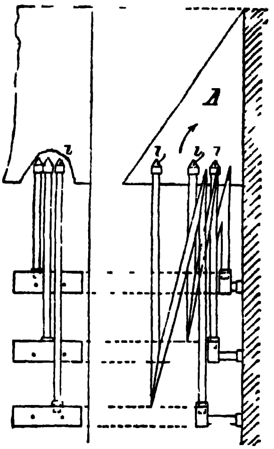


Fig 111

Steger's nozzle, which is used at the Lazy Works, near Beuthen is shown in Fig. 111. The gases and vapours escape from the adapter, first into the lower cylinder *U*, then traverse the sheet-iron tubes a_1, a_2, and a_3, which form the nozzle proper, and escape at the upper end of the latter through the tube *d* into a flue, in which they are burnt and led away. In the tube a^3 discs of iron are arranged, by which the gases are forced to ascend close to the outside circumference of the tube. The zigzag arrangement of the tubes forces the gases to traverse a considerable distance, and at the same time alters their direction repeatedly. The gas is also exposed to the contact of a very extensive surface, and is thus greatly cooled on account of the material of which the tubes consist. The cooling effect is increased by the action of the discs *s*, which force the gas current against the wall of the tube a_3. In consequence of these arrangements, the current of gas is cooled far below its temperature of ignition, so that even should air find its way into the nozzles, explosions are not to be feared. It is said that the amount of zinc fume obtained in this nozzle is very considerable, and greatly exceeds that obtained in the others. The method of arranging this nozzle in Belgo-Silesian furnaces, with several rows of muffles one above the other, is shown in Fig. 112. The gases escaping from the nozzle pass through the openings *i* into the hood *A*, which directs them outwards. As they escape from the openings *i*, they are set fire to and burnt. This nozzle can also be readily applied to Belgian furnaces.



Furnaces for Distillation

The various forms of furnaces are: furnaces with grates, in which the flame rises up, surrounds the muffles laterally, and then escapes, partly through openings in the arch of the furnace, partly through lateral apertures, and furnaces fired by grates or fired by gas, in which the flame rises up to the arch and then returns surrounding and striking the muffles from above, and escaping at the bottom of the furnaces. The furnaces of the former type are known as the old Silesian furnaces, those of the latter type as the Belgo-Silesian furnaces. The Belgo-Silesian furnaces approximate in their construction to the Belgian furnaces when the muffles are arranged in several tiers one above the other, and when the separate muffles are only supported at their extremities in the furnaces like the retorts of the Belgian furnaces. These are used in Belgium, the Rhine Provinces, and Westphalia The old Silesian furnaces were formerly used universally in Upper Silesia, the short-flaming coal, which is there obtainable, being the fuel employed. At present, however, they have everywhere been displaced by the Belgo-Silesian furnaces. The latter, which are suited for coals giving long flames, and for various forms of gas-firing, economise heat to a far greater extent than do the old Silesian furnaces, which nowadays scarcely possess more than historical value.

Old Silesian Furnaces

These are furnaces with a long narrow fire-chamber. In their longitudinal axis a deep grate is built, upon either long side of which the muffles rest upon supports. The flame rising from the grate surrounds the muffles laterally, and then escapes partly through lateral openings in the short side of the furnace into the chambers for calcining calamine, for annealing muffles, and for re-melting the zinc, and partly escapes through a row of flues in the arch of the furnace, either into a main flue leading into a large stack or directly into low stacks. The arrangement of such a furnace is shown in Figs. 113 to 115, in which *b* is the grate; its length is 5 feet 5 inches, and its depth 2 feet 6 inches below the floor of the furnace. It is fired by means of a fire door shown in Fig. 113. Along the two long sides of the grate, or upon their prolongation, 10 muffles are arranged. The roof of the furnace is built of fireclay or of firebricks. Each pair of muffles opens in front into recesses 29 inches high and 26 inches wide, which are known as *chapels*, these being separated from each other by party walls, *Z*, 4 feet 4 inches long and 4 inches thick. The adapters of the muffles lie in these recesses. These furnaces, each of which holds 20 muffles, are built in pairs. After the flame has heated the muffles from the side, it escapes through lateral openings in the shorter walls of the furnace, partly into

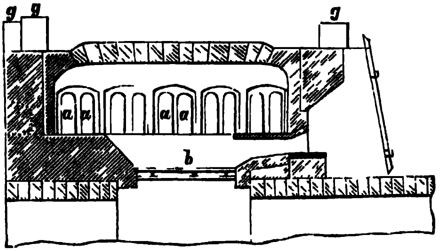


FIG. 113

chambers for calcining calamine, partly into chambers for annealing muffles, and for re-melting the zinc, and then from these into low stacks; *f*,*f* are the calcining chambers built between a pair of neighbouring furnaces, *e* is the chamber for annealing the muffles, and *d* the chamber for re-melting the zinc; *h* is the chamber into which the adapter opens, and in which the zinc collects in the solid form. The front part of this chamber is closed by means of a door during the course of the operation; *g*, *g* are the stacks. The bottom of the muffles in the case of these furnaces lies upon a solid support, and is therefore not struck by the flame.

Furnaces of this kind have been used in England and fired by means of highly bituminous coals. In the arch over the front portion of the muffles there are two rows of holes, whence the products of combustion escape into horizontal flues leading to the stack, no attempt being made to heat annealing or calcining chambers. Each furnace contains 24 muffles. On account of the inefficient utilisation of the heat in these furnaces, 1 part by weight of zinc required for its reduction, from comparatively poor ores, 17 to 20 parts by weight of coal in Upper Silesia; with richer ores and better coals in England 11½ parts of coal. The loss of zinc in Upper Silesia was as high as 30 per cent., and in England amounted to 18 per cent. As already stated, these furnaces have been replaced by the Belgo-Silesian furnaces and are now no longer built.

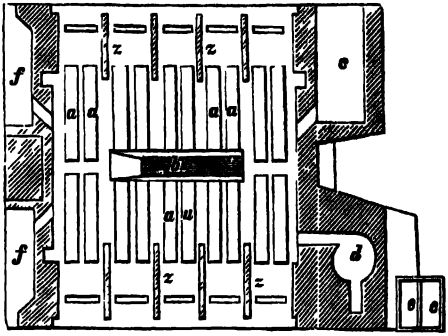


Fig. 114.

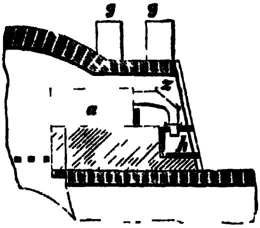


Fig. 115.

Belgo-Silesian Furnaces.

These furnaces have been evolved from the old Silesian furnaces, the flames not being allowed to escape from the furnace either laterally or through the arch, but being first made to strike the arch and then to return, escaping at the bottom of the furnace. Thus the products of combustion escape either through a common flue running under the bottom of the furnace into a stack, or into several stacks, or before entering the latter, they can be utilised for calcining calamine. The muffles rest upon the smallest possible supports inside the furnace, so that even the bottom shall be as far as possible surrounded by flames. In the Rhine Provinces, Westphalia and Belgium, muffles have been made relatively small, arranged in several rows, placed one above the other. By this means heat has been more effectually utilised (6 to 8 parts of coal to 1 part of zinc), the temperature is kept more uniform, the retorts last for a longer time, the output of zinc is greater, and the furnaces can be adapted for a larger number of muffles, and their capacity thereby increased. It was also found possible to avoid the entrance of smoke into the works, and to minimise the injury done by the smoke to the surrounding country.

This method of heating was first introduced at the works of the Vieille Montagne Company in Belgium and Westphalia, flat grates and highly bituminous coals being employed; this is the reason why these furnaces have received the name of Belgo-Silesian furnaces. In the case of the less bituminous coals of Upper Silesia ordinary grates could only be employed, when the layer of fuel was raised up to a considerable height by a bed of clinker, an air blast being forced into the ashpit under the grate, or above the grate at the level of the top layer of fuel. A further improvement was the introduction of gas-firing, which considerably increased the capacity of the furnaces, and has almost completely displaced fire grates. As a rule, therefore, gas-firing should at present be exclusively used for Belgo-Silesian furnaces. In the present state of development of the Belgo-Silesian furnace, we may distinguish furnaces with large muffles lying in one tier as used in Upper Silesia, and furnaces with small muffles in several tiers one above the other, as used in the Rhine Provinces, Westphalia and Belgium. The number of muffles in the furnaces of the first class, which are used only in Upper Silesia, is from 32 to 72. Two furnaces are generally combined to form a block. In the furnaces of the second class, in which there are several rows, usually three, of small muffles, the number of the latter is considerably greater, and may amount to 120. Here also two furnaces are usually built together in one block. For example, at the Munsterbusch Works, near Stolberg, there are 120 muffles in each half of a block, or 240 in the entire block; at Birkengang, near Stolberg, and at the Bergisch-Gladbach Works, there are 216 muffles in a block. It is best to separate the above classes of furnaces into furnaces fired by grates and those fired by gas. Furnaces fired by gas may be divided into furnaces without and with regenerators.

Belgo-Silesian Furnaces Fired by Grates.

Furnaces of this kind were frequently used before the introduction of gas-firing, but have been replaced by gas-fired furnaces at many works. With lean coals, one tier of muffles is used, with highly bituminous coals several, generally two, tiers may be employed. The construction of such a furnace with one row of muffles, as used

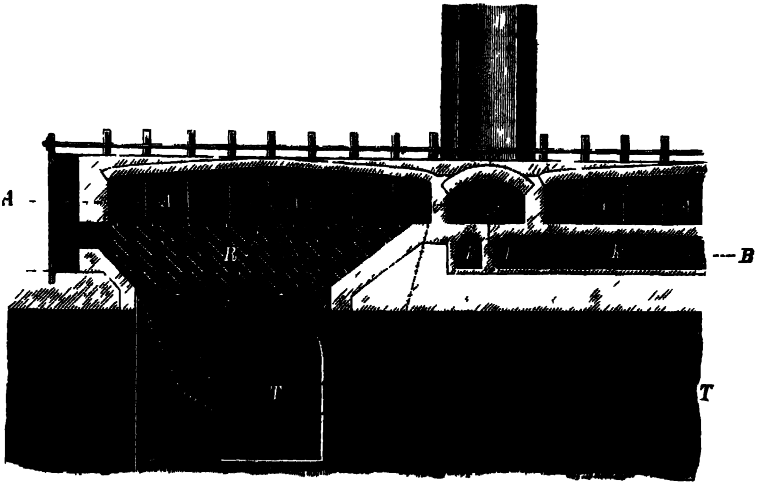


Fig. 116

at Valentin-Cocq, in Belgium, is shown in Figs. 116 to 120. There are 16 muffles *e* on either side of the grate. Two such furnaces are built together, being united by their shorter sides The flame rising through the grate ascends to the arch and then descends, enveloping the muffles from above and escaping through a row of apertures into the flues *k* in the floor, which lead the products of combustion to the stack. In the older furnaces, there are calamine calcining chambers *Z* between each pair, or whenever solid zinc was produced, as in the old Silesian furnaces, chambers for re-melting the zinc, *a*, were also provided. In either case a portion of the flame was diverted through these chambers before entering the stack; *v* are vertical shafts, through which the distillation residues that remain in the muffles are dropped into horizontal arched tunnels *T*. The latter open into a tunnel *w* running parallel to the longitudinal axis of the furnace; *u* are the already-described adapters for the collection of

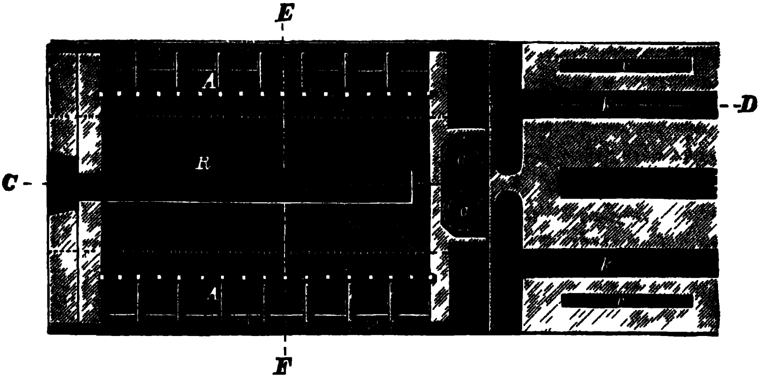


Fig. 117

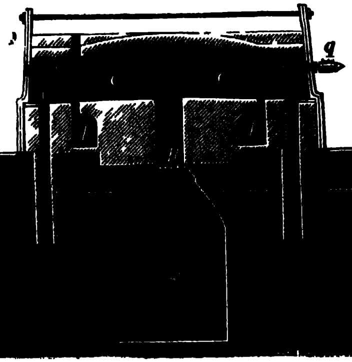
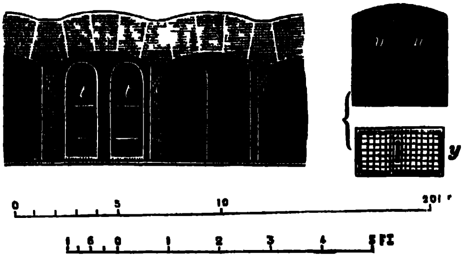


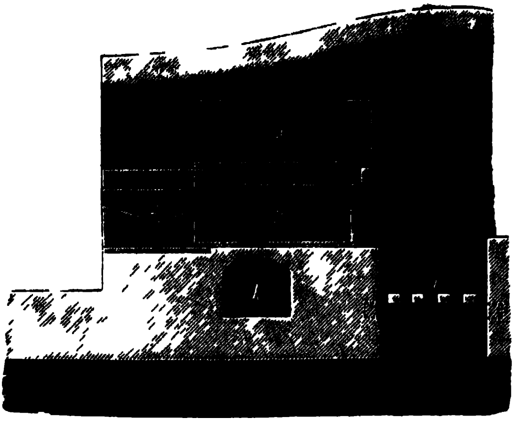
Fig. 118



Figs. 119 and 120

the zinc, *q* the nozzles attached to them for collecting zinc fume. The adapters are arranged in recesses, which have already been considered under the heading of the old Silesian furnaces; *t* are the steps at the front end of the muffles, upon which the rear end of the adapter is supported. The front end of the latter rests in an iron frame which closes the front of the recess. The upper portion can thus be closed, the lower portion being fitted with a tightly shutting door. This form of adapter through which the zinc has to be raked out is often replaced by one or other of the above-described adapters, from which the zinc is tapped out.

In Upper Silesia the muffles also form one tier. On account of the small, non-bituminous coal there available, it was necessary to employ clinker grates with a blast underneath them, or in some cases to use a blast above the top of the fuel. Furnaces of this kind hold from 24 to 28 muffles. The clinker grate is kept 10 inches in height, the blast being produced by means of fans or injectors and conveyed by means of a pipe into the closed ashpit of the grate. When a top blast was used, it was first heated by circulating through flues in the brickwork of the furnace and then entered the grate by means of small apertures. Furnaces of this kind have been replaced in most of the Upper Silesian works by gas-fired furnaces. Gas-fired furnaces with 2 tiers of muffles can only be employed where highly bituminous coals are available, and are in use at very few works. Such a furnace is shown in Fig. 121; *x* are the upper muffles, *y* the lower muffles, *z* the adapters. From the grate, *r*, the flame rises to the arch and descends surrounding the muffles, escaping through the flues *k* below the lower range of muffles into the stack. The upper muffles are 5 inches



longer than the lower ones (5 feet long, 9 inches wide, and 17 inches high). Between each pair of recesses, which are 3 feet deep, there are walls of firebrick.

Belgo-Silesian Furnaces Fired by Gas.

Gas-fired furnaces develop the advantages of the Belgo-Silesian furnaces to a still greater extent; they admit of the employment of inferior fuel and the production of a high degree of temperature, equable heating of a large furnace, and of convenient stoking of the gas producers. On this account the capacity of gas-fired furnaces is considerably greater than that of furnaces fired by grates. They should therefore be used as a rule. The products of combustion either pass directly into the flues or a portion of their heat may first be utilised for calcining calamine and for annealing muffles, or for heating regenerators. Regenerators of the Siemens type are employed. The latter imply, however, a high first cost, careful attendance, and a uniform and not too inferior quality of coal. There is also danger of the flues of the regenerators becoming readily stopped up by zinc oxide and by the carbonaceous matter deposited by the tar, so that in spite of the great advantages of the Siemens furnace it has not found the universal application in zinc works that was expected from it.

Gas Furnaces without Regenerators.

When gas furnaces are employed without regenerators, the air necessary for the combustion of the gases is heated either by passing through flues in the brickwork of the furnace or of the gas producer, or in flues which are surrounded by the escaping products of combustion. When larger muffles are employed, these are arranged in one tier, whereas smaller muffles are generally placed in several. In Upper Silesia, furnaces with one tier of large muffles are employed. These furnaces contain up to 72 muffles. The gas is generated in producers with step grates and led into the furnace through heating flues, at the upper end of which it is burnt by means of a current of air. The air is forced in by means of fans, and is heated in the brickwork of the furnace. The furnace may be worked either by draught produced by a stack, or by a blast underneath the grate, in which case air is also forced into the closed ashpit of the gas producers. The latter arrangement presents the advantage that the inferior small coal and duff may be used for the gas producers. The arrangement of such a furnace with heating flues is shown in Figs.

122 and 123 *G* are the two gas producers, provided with step grates *t*, into the ashpits of which air is blown through tubes *g* The producer gas passes from the producers through flues *l* into the heating flues *h* At the upper end of the latter, the gas is mixed with the heated air required for combustion, which is forced in by means of fans or by

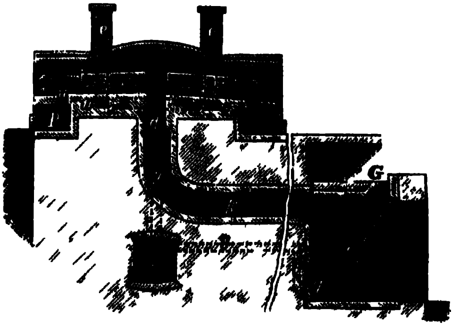


Fig 122

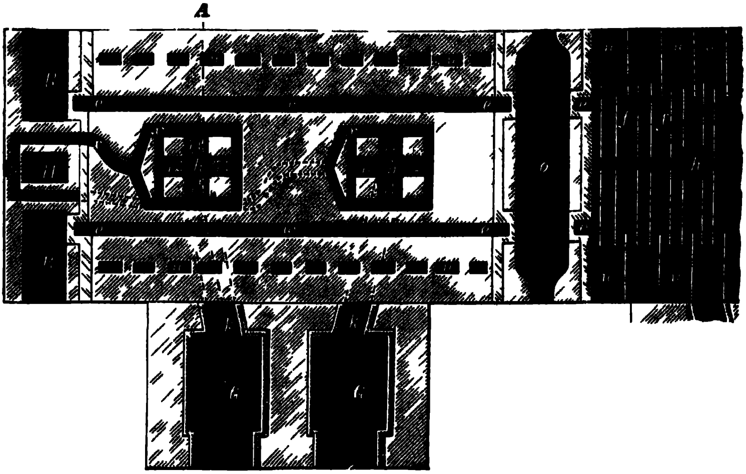


Fig 123

injectors through the flue *z*, from which it passes through the flues *y*, *x* and *x′*, in which it is sufficiently warmed, and escapes through the pipes *d* and *d′*. The flame first rises to the roof and then descends, surrounding the muffles, and escapes through the apertures *f* into the flues *u*, whence the products of combustion pass into the stacks *e*, or into the main stack *H* The blast for the producer is taken from the flue *z* by a branch flue *g*, opening into the ashpit of the producer; *m* are the muffles, *r* are the adapters, *u* are the openings through which the residues in the muffles are dropped into vaults provided with doors; *o* are the calcining chambers built in between each pair of furnaces; *R*, *R* are annealing chambers. A double furnace with 64 muffles as in use at the Hohenlohe Works is shown in Figs. 124 and 125. Fig. 124 is a cross section through the furnace and producer; Fig. 125 a longitudinal section through the furnace. The furnace, which is 53 feet long and 18 feet 6 inches wide, is provided with 2 producers *S*, one to each 32 muffles. The producer gases pass through the flue *K* into 4 vertical shafts *G*, where they are burnt by the introduction of air. This air is forced by means of fans into the flue *Z*, passes from the latter into small flues *x* surrounding the heating flue, and from this through slots *F* into the heating shaft. The heating shaft widens out below into the chamber *u*, so that any flue dust may be collected there. This chamber can be cleaned out through the vault *R*, which is connected by a passage *D* with this chamber. After the flame has heated the muffles, it escapes chiefly through flues *w* at both ends of the furnace into the chambers *M* or *n* for annealing or calcining respectively, and from these chambers through the flues *f* into the stack. Such of the products of combustion as are not required for heating purposes pass directly out of the furnace through the apertures *e* into the stack. *N* are the recesses which contain the adapters of each pair of muffles, *Q* are flues in which any slag collects, that may form when any of the muffles crack. By means of the shafts *v*, the residues from the muffles are thrown into the vault *R*.

Lorenz[1] has proposed a modification of the Silesian gas furnace in which the gases and air do not enter through the floor of the furnace, but through its two end walls. The flames thus enter from either side of the furnace, pass between the muffles towards the centre, where they meet, surrounding the muffles and returning along the sides of the furnace to the end walls, whence they escape into flues. The construction of such a furnace with small muffles arranged in 2 tiers, and heated by gas generated in a Boetius producer, is shown in Figs. 126 and 127.[2] The air used for combustion is heated in the flues *l* of the well-known Boetius producer, this air mixing at *o* with the gases ascending from the producer. The flame first rises to the roof and then descends through the flues *a*, which are built between each pair of recesses, into the flue *b*, which conducts the

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[1] D. R. Patent, No. 10,010, October 21, 1879.

[2] *Oesterr. Zeitschr.*, 1881, p. 336.

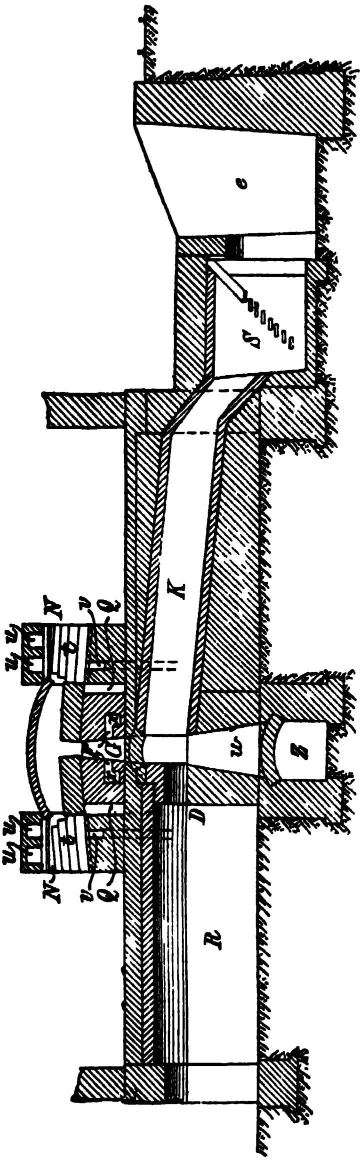


Fig 124

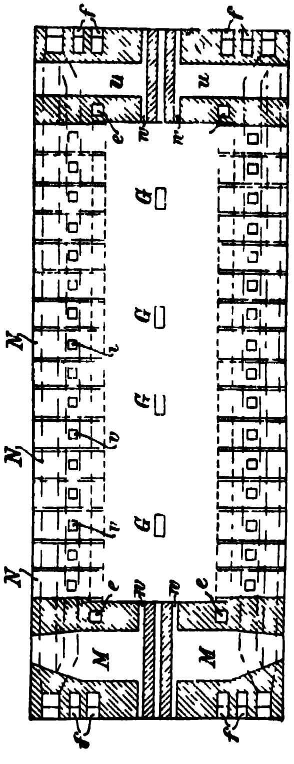


Fig 125.

products of combustion to the stack; *m, m* are the muffles placed in two tiers one above the other. The residues from the distillation are dropped into the shaft *R*; when these residues are being drawn out from the lower muffles, the tiles that close the upper portion of the vertical flues are removed, and when the residues have to be removed from the upper muffles, the tiles *R′* are removed also. The

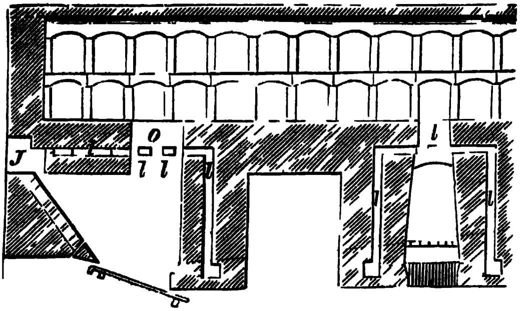


Fig 126

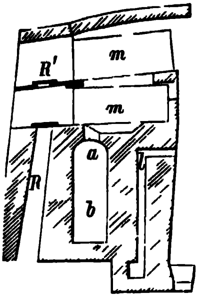


Fig 127

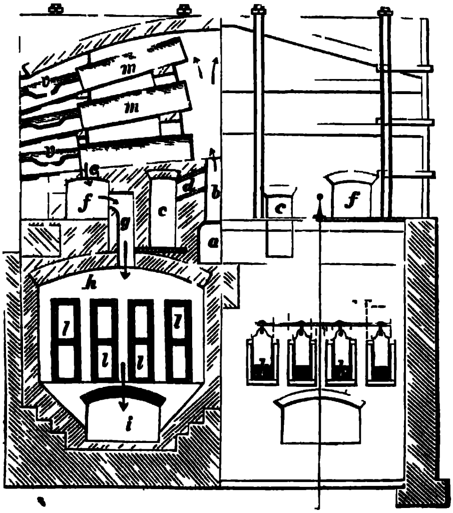
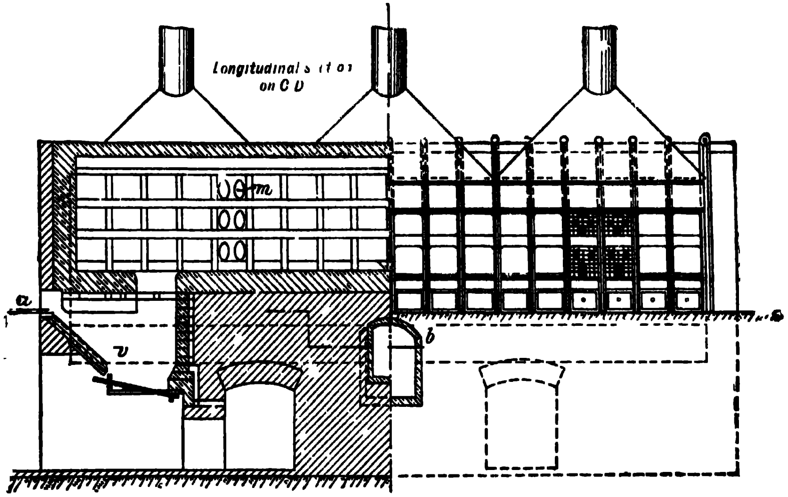


Fig 128

Boetius producer has given satisfactory results, and is being successfully used at the works in the Rhine Provinces.

Fig. 128 shows the construction of a furnace with 3 tiers of muffles; *m* are the muffles, *v* are the adapters; the lowermost muffles lie for their full lengths upon the hearth and project for some 2 inches into the recesses. The muffles of the 2 upper tiers are also supported in front in the recesses, their back ends lying upon supports made of exceedingly fireproof material. The gas which is developed in the producer, not shown in the figure, enters through the flue *a* into the vertical shaft *b*, at the upper end of which it is burnt by means of hot air there introduced from the outside through the flues *l*. The quantity of air can be regulated by means of dampers, *k*, at the mouth of the latter. Through the flues *l* the air passes into the flue *c*, and from the latter through *d* into *b*. The flame rises first to the roof, and then returns, escaping through apertures *e* into the flue *f* thence through the vertical flue *g* into the large horizontal flue *h*, and from the latter into the flue *i* leading to the stack. In its passage through the flue *h* the



FIGS 128*a* AND 128*b*

products of combustion surround the air flues *l* and thus heat the air to be used for combustion. These furnaces contain 50 to 55 muffles, and are in use in the Rhine Provinces.

The construction of a furnace of the most recent type with oval muffles, such as are at present in use in the Rhine Provinces, is shown in Figs. 128*a* to 128*e*,[1] Fig. 128*a* being a longitudinal section on *c d*, Fig. 128*b* a front elevation, Fig. 128*c* a cross section on *e f*, Fig. 128*d* a sectional plan on *a b*, and Fig. 128*e* on *g h*. The muffles are of the pattern now generally used in the Rhenish and Westphalian zinc works; they are oval in cross section and are made by machinery as already described; in this furnace they are arranged in three tiers, there being 108 in each side of the furnace block, or 218 in all. The adapters are shown at *v*, Fig. 128*c*. There is a gas producer *v*, Figs. 128*a* and 128*d*, at each of the short sides of the furnace; the air for the combustion of the producer gas undergoes previous heating in the walls of the producer as indicated in the figures. The products of combustion, after heating the muffles, escape through the vertical flues *w* into the main flues *z* which communicate with the stacks.

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[1] Durre, *Ziele und Grenzen der Elektro-metallurgie*, p. 207, Leipzig, 1896.

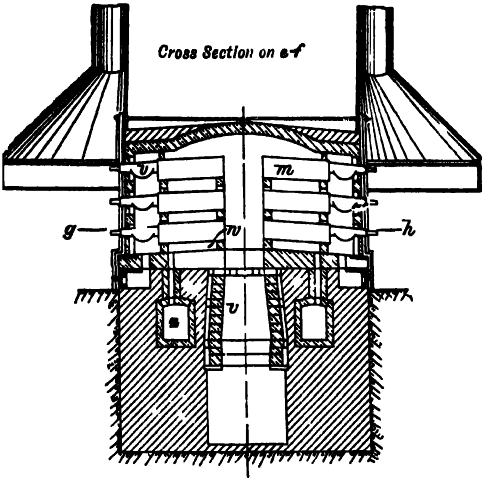
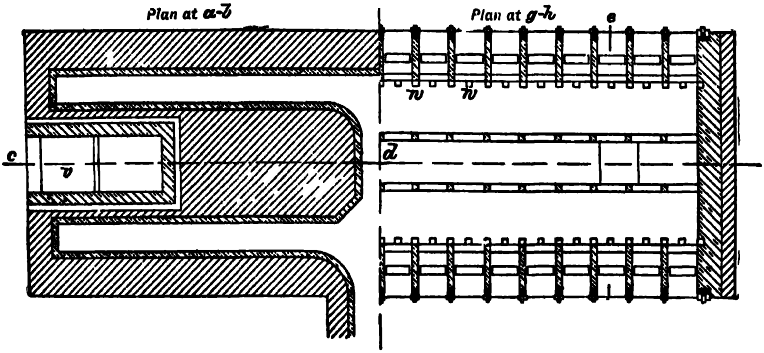


FIG. 128



FIGS 128*d* AND 128*e*

Gas Furnaces with Regenerators.

Furnaces on the Siemens principle are used in Upper Silesia, in Freiberg, in Cilli (South Austria), and in the Rhine Provinces. They require coal which shall not be in too small pieces. They admit of the uniform heating of large chambers to a very high degree of temperature, and in consequence thereof cause an economy of fuel and of muffles, and permit of longer campaigns than in the case of furnaces working without regenerators. On account, however, of their high first cost, of the necessity of employing better qualities of coals, of the care required in their management, of the readiness with which the flues in the regenerators become stopped up, of the difficulties connected with their heating, and of the high consumption of fireproof material caused by the regenerators, the application of the Siemens principle to distillation furnaces has been greatly limited, in spite of the above-named advantages. The general construction of a zinc distillation furnace on the Siemens

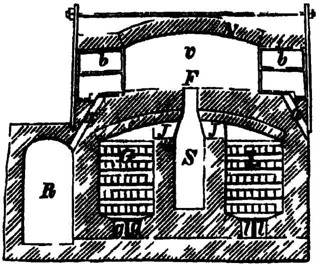


FIG. 129

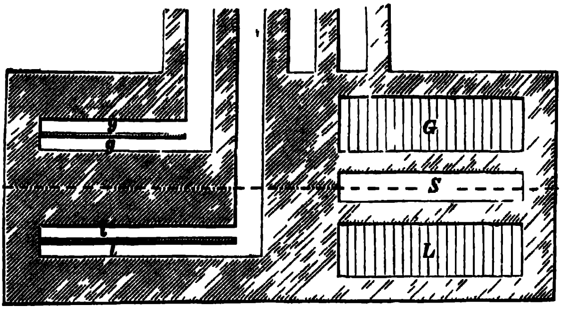


FIG. 130

principle is shown in Figs 129 and 130. *L* are the air regenerators, *G* the gas regenerators, *g*, *g* are the flues for the admission of gas, and *l*, *l* for the admission of air to their respective regenerators The gas and air, after being heated, pass through flues, *J J*, into the mixing chamber *F*. The flame ascends first in one half of the heating chamber *v* up to the roof *N*, then enters the other half, where it descends, passing finally to the regenerators, which it traverses, and then escapes to the stack The distillation residues from the muffles are dropped through the inclined shafts *a* into the vaults *R*. *S* is a pocket for the collection of flue dust, *b* are iron frames which replace the partition tiles of the recesses They were designed by Cochlovius,[1] and are shown on a larger scale in Figs. 131 and 132 (each pair of recesses is otherwise separated by fireclay tiles 2 inches thick, known as partition tiles) The front side *a b* of the frame is secured to the buckstaves of the furnace, whilst the back portion *c d* sets

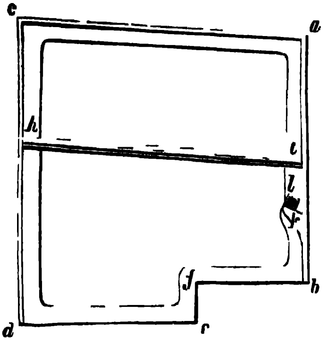


Fig 131

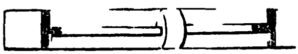


Fig 132

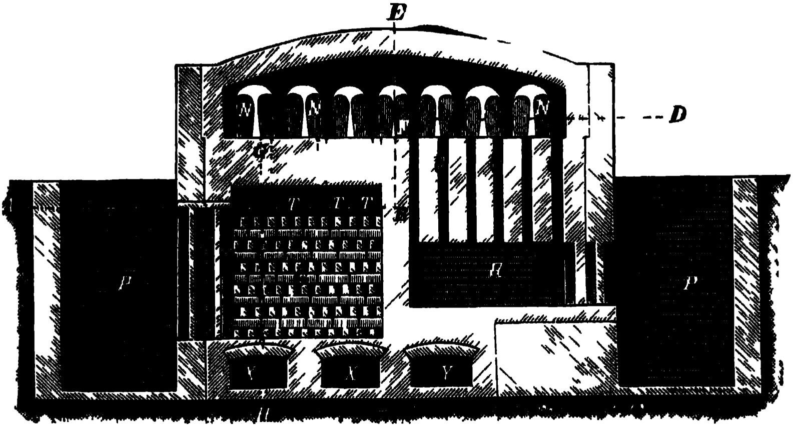


Fig 133.

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[1] D R Patent, No. 9,128.

against the furnace itself. The arch is carried by the upper portion *a c* of the frame. Of the lower portion of the frame, the portion *d e* is let into the furnace, whilst *e f* lies against the floor of the furnace. A cross-bar *h i* serves to stiffen the frame. An iron rail lying upon a projection *k* replaces the step upon which the front portion of the adapter rests.

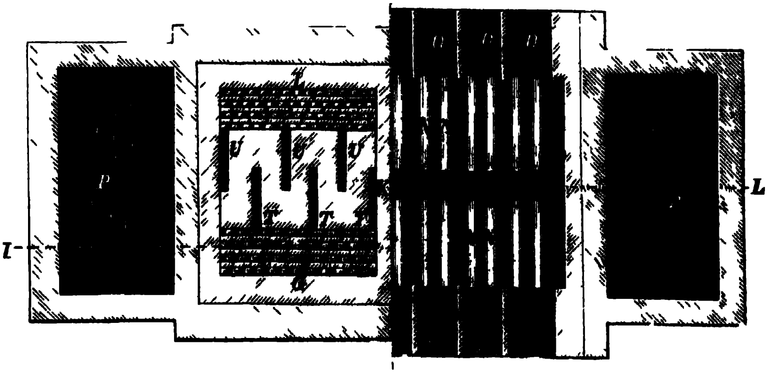

FIG. 134

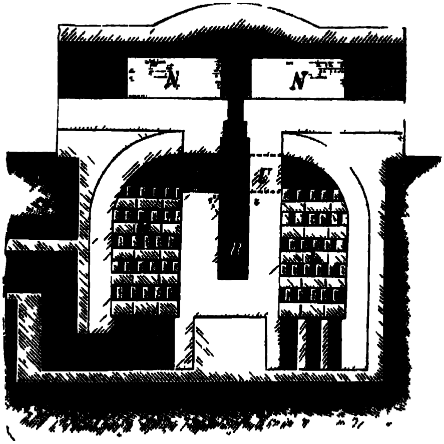

FIG. 135

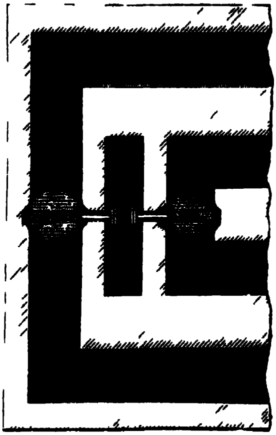

FIG. 136

The construction of the older zinc distillation furnaces at Freiberg is shown in Figs. 133 to 137. The regenerators lie under the furnace, and parallel to its longitudinal axis. *L* is one of the air regenerators, *G* one of the gas regenerators. The other pair of regenerators lying beneath the other half of the furnace is not visible in the figure. *W* is the reversing valve for the gas and *W'* for the air current. *X* are the gas flues, *Y* the air flues. The gas passes through *X* into the regenerator *G*, the air through *Y* into the regenerator *L*. At the upper portion of the regenerator the gas escapes heated through 3 flues into corresponding vertical slots, whilst the air escapes at the upper end of the air regenerator through an equal number of flues *U* into its corresponding vertical slots. At the top of these slots the air and gas mix, the flame thus produced first surrounding 2 tiers of muffles on one side of the furnace, and then passing into the second half of the furnace, where it surrounds the muffles therein contained, and then escapes through the six air and gas slots in the floor of the furnace into the corresponding regenerators, from which it passes to the flue *E*, and thence to the stack. At definite intervals—from half an hour to an hour—the direction of the air and gas currents is reversed by means of the reversing valve, so that gas and air now ascend in the second half of the furnace, first heat the muffles contained therein, and then take their way through the first half of the furnace to the first pair of regenerators, whence they escape to the stack. The air and gas slots are prolonged downwards into chambers or pockets *R*, into which any flue dust drops down, and collects. By means of the chambers *P* the brickwork which forms the outer wall of the regenerators and pockets is accessible, so that these can be repaired and cleaned out when desired. *N* are the muffles, *O* are the recesses. The number of muffles in single furnaces of this kind amounts to 28 to 32, in double furnaces to 56 to 64. A furnace of this kind with several tiers of muffles one above the other, is arranged similarly to that described under Gas Furnaces without Regenerators. Furnaces on the Siemens principle have been used with good results at the Paul and Wilhelmina Works, near Schoppinitz. The gas furnace with air regenerators of Haupt,[1] which are provided with regenerators along each side of the longitudinal axis of the furnace, do not seem to have come into use.

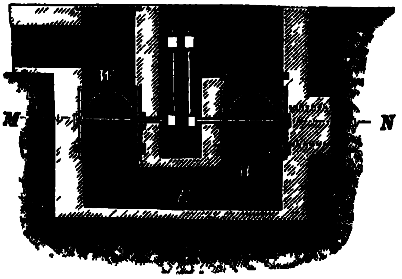

FIG. 137.

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[1] D. R. Patent, No. 7,425, *Oesterr. Zeitschr.*, 1881, p. 336.

The Charge

The charges for muffles are prepared in the same way as for retorts; calamine is not, however, submitted to distillation in the form of powder, but in pieces of the size of a hazel nut, so that the muffle charge, which is very much larger than that for the retort, shall not be too compact. Binon and Grandfils[1] have also proposed the employment of charges mixed with tar and moulded into blocks for muffles. According to their views, by the employment of blocks moulded to the shape of the muffle, 50 per cent. more charge can be introduced into it than by the ordinary method of charging. It is also claimed that in this case the reduction takes place at a comparatively low temperature. As far as is known, however, these proposals do not seem to have received any practical application. In Upper Silesia the coal used for reduction is employed in the form of what is known as *cinder*, that is to say, after its gas has been got rid of. This cinder is obtained partly from puddling works, partly collected below the grates of the gas generators, and partly produced in special furnaces. For instance, at the Hohenlohe, Kunigunde and Theresia Works, in Upper Silesia, coals of grain and pea size are heated in furnaces, whereby they partly coke and may agglomerate a little, according to their quality. At the Paul and Wilhelmina Works near Schoppinitz, coals thus heated are also partially employed. In many works crushed coke is used. By driving the gas off from coals, from 63 to 72 per cent. of the weight of the latter is obtained as cinder. Of recent times the quantity of cinder in the charge in Upper Silesia has been continually on the increase; by these means the red-hot particles of coal in the charge are brought into intimate contact with the ores, and the formation of an atmosphere of carbon monoxide is at the same time promoted, so that any oxidising influence of carbon dioxide, water vapour and air are prevented from affecting the zinc vapour. For example, at the Wilhelmina Works, the proportion of cinder amounts to almost 50 per cent. of the weight of the ore treated, or 34·9 per cent. of the total fuel used in the operation. The charge for one muffle is at present about 2 cwts. on the average for Upper Silesia, and 60 to 77 pounds in Belgium, the Rhine Provinces and Westphalia.

Process of Distillation

Before a furnace is put into operation, it is carefully dried and fired up slowly. In the case of the old Silesian furnaces, as soon as the furnace has attained the requisite temperature, the muffles which have been raised to a red heat in the annealing furnace are set in their places. *The interspaces between the muffles and the columns are filled in with bricks and clay. The adapters are then attached* to the muffles, and the openings in the lower portion of the muffle below the adapters are closed by the tiles previously mentioned. The charges are then gradually introduced through an opening in the bend of the adapter by means of a long scoop, which passes through the horizontal portion of the adapter into the muffle. The charge of the muffles, small at first, is gradually increased, until on the seventh day they are taking their full charge. The muffles that lie nearest the fire are more heavily charged than those farther away from it. After the muffle has been charged, the opening in the bend of the adapter is closed by means of a tile luted upon it; the sheet-iron doors in front of the recesses are closed; and the temperature of the furnace is raised to whiteness. Soon after the introduction of the charge, under ordinary circumstances, carbon dioxide, carbon monoxide and water vapour are evolved, and zinc fume is deposited in the adapters as a result of the action of carbon dioxide and water vapour upon the zinc vapours, as also of the high degree of dilution of the latter by the above-named gases; in order to prevent the adapter from being clogged, it must be repeatedly cleaned out. Two to three hours after the charge has been introduced, carbon monoxide alone is contained in the escaping gases. As there are now no oxidising agents present, and as zinc vapour is contained in large quantities in the gas, condensation of zinc commences, attains its maximum after 6 to 8 hours, and remains stationary for another 6 to 8 hours. It then diminishes, and is concluded in a few hours longer. The total time of working off a charge, including charging, occupies 24 hours. When the distillation is complete, the front doors of the recesses are opened, and the tiles are removed from the charging openings. Any fluid zinc that may still be remaining in the horizontal portion of the adapter is raked down into the condensing chamber, and the metal that is solidified in the latter is removed. The tile which closes the muffle below the step supporting the adapter is now removed by means of tongs and the residues of the distillation are drawn out by means of scrapers, any accretions upon the sides of the muffles being knocked off by means of an iron bar. Muffles that have become defective are changed, and others which may have been cracked, but which are still capable of being repaired, are luted with clay. The muffles are then charged afresh. The two rows of muffles are either charged one directly after the other or else the second row is charged some time, up to 8 hours, after the first, in order to give the workmen time for a rest. By the latter method, the uniform course of the process and the output of zinc are interfered with.

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[1] *Berg. und Hutt. Ztg.*, 1883, p. 198-211; 1882, p. 531; 1881, p. 27.

The process of distillation when Belgo-Silesian furnaces are employed agrees with the former, except as influenced by the different construction of these furnaces as regards the disposition of the muffles and the character of the adapters. The furnaces are heated up by means of a coal fire maintained upon the grates or in the gas producers. Furnaces on the Siemens principle are not heated up by means of the producer, but by means of a fire maintained upon a provisional grate inside the furnace itself. These grates are arranged in two recesses lying diagonally opposite to each other, whilst the other recesses are loosely bricked up during this period of heating up. After three or four days the muffles are put into their places, and annealed in the furnace itself. After the fire has been gradually increased for another three or four days, the grates are removed and gas is introduced from the producer, which has been carefully warmed up and fired, the requisite quantity of air for burning the gas being at the same time admitted. After gas-firing has thus been commenced, muffles previously heated to a red heat are introduced into the two recesses, which have now been set free for this purpose; the muffles are then bricked in, the adapters are attached, and the muffles charged. In the case of adapters of the bellied form, charging takes place through the front of the adapter, whilst with those having the shape of inclined cylindrical tubes or of rectangular boxes, the front of which is closed by a tile, or by a clayed iron plate, charging is performed through the apertures left when these plates are removed. If there are several tiers of muffles, the topmost tier of muffles is charged first. The first charges are very small and consist of readily reducible material, such as zinc fume and rich residues, the charges being gradually increased up to the normal. The time of working off a charge in this furnace amounts also to 24 hours. The temperature must be kept as uniform as possible during the process of distillation. Should it be too high, uncondensed zinc escapes through the adapters and burns in contact with the air; if it is too low, the zinc condenses as fume, which partly remains in the adapters, and partly is carried off by the current of gas. In such a case the adapters in the old Silesian furnaces might possibly become stopped up by solid zinc. If any of the muffles crack, zinc vapour may either escape from the muffles into the furnace, or the furnace gases may enter the muffle, according to the ratio between the pressures inside the furnace and inside the muffle respectively. After the conclusion of distillation, zinc is removed from the adapters, the residues are then raked out, the muffles are repaired or replaced, and then charged once again. Zinc is raked out from the bellied adapters and collected in a ladle held beneath the latter. From the inclined cylindrical or rectangular adapters the metal is tapped out into iron ladles by removing the front plate. By means of these ladles, which are provided with spouts, the fluid zinc is cast into moulds. When several tiers of muffles have to be dealt with, the zinc is first collected from the uppermost tier of muffles.

ECONOMIC RESULTS AND EXAMPLES OF ZINC EXTRACTION IN MUFFLES

OLDER FURNACES FIRED DIRECT

Old Silesian Muffle Furnaces

In Upper Silesia by means of old Silesian furnaces with 20 muffles in each, 15 cwts. of calamine were treated in 24 hours, in furnaces with 24 and 26 muffles, 18 and 20 cwts. of calamine respectively. The output of zinc from the ore amounted to 14·07 per cent. For the production of 1 cwt. of zinc, 7¼ cwts. of calamine, and 35 cwts. of coals were required.

The muffles lasted 6 to 8 weeks.

Belgo-Silesian Furnaces Fired by Grates

At Valentin Cocq, in Belgium, furnaces were employed with 24 muffles 4 feet 4 inches long, 22 inches high and 8¾ inches wide, as also furnaces with 32 muffles, 4 feet 7 inches long, 23⅝ inches high and 8¾ inches wide. The charge of the former amounted to 1280 lbs. of calamine and 3 cwts. of coal for reduction. This charge was treated in 24 hours, and required 36 cwts. of coal, about 8 cwts. of coal being consumed to 1 cwt. of zinc. The consumption of muffles amounted to 0·41 and of adapters to 2 in 24 hours. The 32-muffle furnaces received a charge of 2028 lbs. of calamine and 507 lbs. of coal for reduction, the fuel consumed in 24 hours being 4724 lbs. = 6·14 cwts. for each cwt. of zinc. The consumption of muffles per furnace per 24 hours amounted to 0·40, and of adapters to 2·4. At Letmathe, near Iserlohn, where blende is chiefly smelted, there are at present (1895), furnaces in use with a combined step grate and flat grate, which contain each 75 oval muffles 6½ inches broad and 10 inches deep in the clear; (furnaces on the Siemens principle were used, but have been discontinued). To each cwt. of calcined ore 42 to 44 lbs. of coal in the form of anthracite is added. The charge of a muffle amounts on the average to 57 lbs., the period of distillation amounting to 23 hours. A furnace with 75 muffles treats in 24 hours 1 ton 19 cwts. of calcined ore. For each cwt. of zinc 3 to 4 cwts. of fuel and 1¼ cwts. of coal for reduction are employed. The loss of zinc amounts to 14 to 16 per cent. For a cwt. of zinc 0·4 cwt. of muffles are consumed. The labour employed per 24 hours amounts to 1 shift of 24 hours and 2 shifts of 10 hours.

At the Silesia Works, near Lipine,[1] the older furnaces, working with flat grates and blast in the ashpit, contained each 24 muffles, 21·6 inches high and 7·2 inches broad. The charge of a furnace amounted to 4116 lbs., yielding an output of 917 lbs. of zinc per 24 hours. For each cwt. of zinc, 48 cubic feet of coals and 0·10 muffle were consumed.

Belgo-Silesian Furnaces Fired with Gas

Here we have to distinguish between furnaces with large muffles in one tier used in Upper Silesia, and furnaces with several tiers of smaller muffles one above the other, as used in Belgium, the Rhine Provinces and Westphalia. Modern furnaces in Upper Silesia with a single tier of large muffles, fired by gas, consume at present some 10 cwts. of coal, of which 7 cwts. is used as fuel, for each cwt. of zinc produced, the charge containing 20 per cent. of zinc, and the average weight of charge to each muffle being 227 lbs. The weight of coal used for reduction amounts to about 40 per cent. of the weight of the ore, or about 2·8 cwts. per cwt. of zinc. Of this coal, 1 cwt. consists of cinders or of coke from the gas producers. In 1870, the consumption of coal amounted to 19·16 cwts., and in 1880 to 12·41 cwts. per cwt. of zinc. Rather less than 4 cwts. of clay are consumed to each ton of zinc. For each 13 or 14 muffles 1 workman is required per 24 hours, or 4 to 5 men for the production of 1 ton of zinc in this time. The loss of zinc amounts to 25 to 30 per cent. The residues of distillation contain 3 to 3·5 per cent. of zinc. Of the above loss, 12 to 15 per cent. is due to the zinc retained in the residues and 10 to 15 per cent. to volatilisation. Each muffle yields 10 to 12 cwts. of crude zinc.

The modern Silesian furnaces in Belgium, the Rhine Provinces and Westphalia, the Belgo-Silesian furnaces proper, consume 3 to 4 tons of coals for reduction and fuel, and about 4 cwts. of clay to each ton of zinc, employing ores containing 50 per cent. of zinc, and a charge of 75 lbs. in each muffle. One man is required for every 13 to 14 muffles per 24 hours = 4 to 5 men per ton of zinc in this period. In the older furnaces, 6 to 7 tons of coals used to be consumed for each ton of zinc produced. The loss of zinc varies from 9 to 15 per cent.

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[1] *Berg. und Hutt. Ztg.*, 1867, p. 340.

At the Hohenlohe Works, in Upper Silesia, where single storied furnaces, shown above in Figs. 124 and 125, with 32 muffles are used, each 22 inches high, 6 inches wide, 4 feet 9 inches long over the gas shafts, the others being 5 feet 5 inches long, the charge consists of 17 cwts. of calcined blende, containing 42 to 45 per cent. of zinc, 5 cwts. of calamine in small pieces, containing 26 to 32 per cent. of zinc and 21 cwt. of calamine slimes, containing 14 to 16 per cent. of zinc, or altogether 2·3 tons of ore; the yield in 24 hours amounts to 1080 lbs. of zinc During this period 3 tons 7 cwts. of coal were consumed in the process, or 6·83 lbs. of fuel to the lb. of crude zinc.

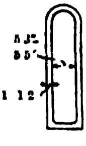

FIG. 139.

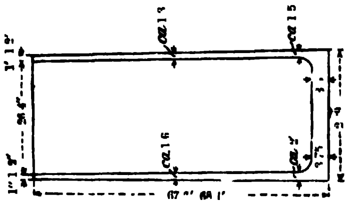

FIG. 138

At the Silesia Works, near Lipine,[1] there are at present (1895) furnaces in use, which are built with 2 gas shafts, to carry 32 to 40 muffles, 16 or 20 respectively on either side. There is a separate producer to each furnace. The air employed for combustion is blown in by means of a fan and mixed with gas, 1 foot 8 inches below the upper edge of the shafts. The dimensions of the muffles and their thicknesses are shown in Figs. 138 and 139. The mixture of which the muffles are composed consists of 37 to 40 parts of raw clay and 60 to 63 parts of fragments of muffles and burnt clay shale. The raw clay is obtained partly from Briesen, in Moravia, partly from Saarau, in Silesia. The clay shale is obtained from Neurode and Mittelsteine, in Silesia. The fragments of muffles are obtained by grinding old muffles down to a mesh of 0·23 to 0·27 inch. The charge consists of 25 to 45 parts of calamine and 75 to 55 parts of calcined blende, according to the quantities of these respective ores that may happen to be available. The reducing agent consists of cinders, the quantity of which amounts to 45 to 47 per cent. of the weight of the ores. The charge for a muffle amounts to 198 lbs. The period occupied in distillation is 16 to 17 hours, that for the remaining operations 7 to 8 hours. A muffle will last between 35 and 47 days, depending chiefly upon the age of the furnace, and therefore upon the greater or lesser solidity of the muffle seat, and upon the ratio of zinc blende contained in the charge, zinc blende requiring a higher temperature than calamine. The output of a furnace in 24 hours amounts to 6,350 lbs. of ore for 32 muffles, and 7,940 lbs. for 40. The consumption of fuel per ton of ore varies from 1 to 1·2 tons; per ton of zinc it amounts to 5·5 tons. The fuel used is partly duff, partly very slaty coarse coal; the consumption of reducing agent amounts to 2 tons per ton of zinc, and the consumption of muffles to 2 per ton of zinc. The output of zinc is 77 to 80 per cent. of that present in the ore, or 20 per cent. of the weight of the latter. The loss of zinc varies from 20 to 23 per cent.

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[1] Kindly communicated by the factory inspector, Scherbening, of Lipine.

At the Paul Works, near Rosdzin, there are at present (1895) in use Siemens furnaces and gas-fired furnaces using blast in the ashpit. Each furnace has its own producer and one or two heating shafts. The number of muffles amounts to 32. Air is introduced below the grate of the producer by means of a fan in order to generate gas, as also under the body of the furnace to burn the gases. The muffles are made of a mixture of 65 per cent. of clay and 35 per cent. of muffle fragments. The ore mixture contains 30 per cent. of calcined blende and 70 per cent. of calcined calamine; the reducing agent—cinder—amounts to 40 per cent. of the weight of the ore. Each muffle takes a charge of 2 cwts. The time required for treating a charge, including recharging the muffles, is 24 hours. The muffles will stand from 40 to 50 days. A furnace with 32 muffles will treat on the average 3 tons of ore in 24 hours, extracting 8 to 10 cwts. of zinc. The consumption of fuel in this time amounts to about 4 tons, = 1·33 tons of coal per ton of ore, or 8 to 10 parts of coal to 1 part of zinc. The output of zinc is about 13 per cent. of the weight of the ore, the loss of zinc amounting to 21 per cent.

At the works of the Berzelius Company, near Gladbach, there are 3 tiers of small muffles; a furnace block holds 208, which are emptied every 24 hours, there being 12 men engaged during that time. The charge consists of calcined blende, containing 52 per cent. of zinc, and of cinder. Each muffle receives a charge of 55 pounds of ore and 18 pounds of cinder. The charge for the furnace amounts to 5·2 tons of ore and 1·664 tons of cinder, the output per 24 hours amounting to 2·4 tons of zinc, with a loss of 10 to 13 per cent. Muffles will last from 45 to 60 charges. For each cwt. of zinc 3·9 cwts. of coal for fuel and for reduction are consumed.

At the Neumühl-Hamborn Works, near Oberhausen, furnaces are employed with producers in which the air is heated. These furnaces are double furnaces containing on each side 3 tiers of muffles, each row containing 42 muffles, and each side of the furnace 126, so that the entire furnace takes 252 muffles. Each such furnace has 2 producers, one at either end. The muffles are upon the average 4 feet 7 inches long, 6¼ inches broad and 12 inches high in the clear, and are made of a mixture of about 30 parts of calcined Belgian clay, 35 parts of raw Belgian clay, and 5 parts of coke. The charge consists chiefly of calcined blende, containing 53 to 55 per cent. of zinc. The coal used as a reducing agent, amounting to 40 to 42 per cent. of the weight of the calcined ore, consists of coarse siftings from the lean coal of the basin of the Ruhr. The charge for a muffle consists of 66 to 73 pounds of ore and 29 pounds of coal, as also of a small quantity of skimmings and residues. The total charge for a double furnace consists of 7·6 to 8 tons of ore, exclusive of the skimmings and residues of the previous day. The distillation lasts 19 hours, 5 hours being employed in cleaning up and charging. The consumption of fuel amounts to 12 tons per furnace per 24 hours; this fuel is a coal slack giving a long flame and containing 22 per cent. of ash. With a good quality of coal, such as is being used in other works in the Rhine Provinces and Westphalia, one third less coal would be required. For each ton of zinc 3·6 tons of coal are used for fuel and 0·88 for reduction. A muffle lasts 30 days on the average, 8 muffles being destroyed per day per furnace. During 6 hours in which the muffles are being emptied and recharged 12 men are engaged; during the period of reduction 2 men, who work a 12-hour shift.

Furnaces with Regenerators

Furnaces are in use, both on the Siemens principle with gas and air regenerators, as also furnaces with air regenerators only. The distillation furnace at Freiberg, on the Siemens principle, has 32 muffles disposed in two rows of 16 each; they are 5 feet 2 inches long, 9¼ inches wide, and 19¼ inches high. The charge for a muffle consists of 1 cwt. of calcined blende, containing 33 per cent. of zinc, and 25 per cent. of lignite coke. The process of distillation lasts 24 hours, the consumption per cwt. of blende amounting to 5·3 cubic feet of fuel. The weekly output of the furnace is 2½ tons of zinc and 5 cwts. of zinc fume, containing 90 per cent. of zinc. The output of zinc amounts to 70 per cent. The distillation residues contain 10 per cent. of zinc; they carry silver and are smelted with lead for the extraction of the silver.

At the Birkengang Works, near Stolberg, furnaces on the Siemens principle are now in use (1895) containing 3 tiers of muffles. They are built together in pairs, their longer sides adjoining. Each row consists of 18 muffles, so that the double furnace contains 54 muffles on either side or 108 altogether. The charge consists chiefly of blende, and contains 52 to 53 per cent. of zinc, 37 to 38 per cent. of lean coal being added as a reducing agent. The total ore charge of a double furnace amounts to 4·9 tons. The distillation lasts 24 hours, 1·2 tons of fuel being consumed to each ton of ore. The men employed per furnace per 24 hours number 10; they work 12-hour shifts. A muffle, composed of two-thirds of burnt and one-third of raw clay, lasts on the average 40 days.

At the Paul Works, near Rosdzin, Siemens furnaces are used carrying 60 to 72 muffles, 5 feet 7 inches to 5 feet 11 inches long. Two producers are attached to each furnace. The muffles are made of a mixture of 65 per cent. of clay and 35 per cent. of fragments of old muffles. The ore charge consists of 30 per cent. of blende and 70 per cent. of calamine, the reducing agent—cinder—amounting to 40 per cent. of the weight of the ore. The charge for a muffle consists of 220 to 242 pounds. The total period of distillation, including the necessary operations, amounts to 24 hours. A muffle lasts 40 to 50 days on the average. A furnace with 60 muffles treats 6 tons of ore in 24 hours, extracting about 1 ton of zinc. The consumption of fuel during this period amounts to 6·1 tons, = 1·016 ton per ton of ore, or 6·1 tons per ton of zinc. The consumption of cinder for reduction amounts to 8 cwts. per ton of ore, or 2·4 tons to the ton of zinc. The consumption of muffles amounts to 1·35 per ton of zinc. The output of zinc is 13 per cent. of the weight of the ores. The Siemens furnaces require a better quality of fuel than is needed for ordinary furnaces using blast in the ashpit; the former, however, work more uniformly and consume less fuel than do the latter. The advantages of the Siemens furnace are shown from the following table of the working results of the grate-fired furnace and the Siemens furnace at the Paul Works for the year 1895:—

	Grate Furnace with 82 Muffles. tons.	Siemens Furnace with 60 Muffles. tons.
Ore treated per furnace per 24 hours . . .	3	6
Consumption of fuel per ton of ore . . .	1·33	1·016
Consumption of muffles per 5 tons of ore .	1·6	1·0
Percentage of zinc extracted from the ore .	13	13

At the Cilli Works,[1] a furnace on the Siemens principle contains 136 muffles. These muffles, made of a mixture of one-third of raw and two-thirds of burnt clay, are 16½ inches high and 8 inches wide. The charge for each muffle amounts to 77 lbs.; the reducing agent consists of a mixture of cinder and lignite from Fünfkirchen. The fuel is a mixture of coal and lignite. There are three producers to each furnace. Distillation lasts 24 hours, and the zinc contents of the residues amount to 4 to 5 per cent.

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[1] *Berg. und Hütt. Ztg.*, 1884, p. 31.

At Stolberg there are furnaces which have regenerators for air only. At the Birkengang Works furnaces with air regenerators are in use (in 1895). Like the Siemens furnace in use in the same place each half of the double furnace contains three tiers of 18 muffles each. The charges, the practical results, and the process are the same as in the case of the Siemens furnace.

At the Münsterbusch Works, near Stolberg, furnaces are also at work (in 1895) provided with air regenerators. To each furnace block there are two producers, one at either end. There are three tiers of muffles of 80 each, or 240 altogether. The latter are 4 feet to 4 feet 7 inches long, and take a charge of 75 lbs. of calcined ore and 31 lbs. of coal. They are made of a mixture of 60 per cent. of burnt and 40 per cent. of raw Belgian clay, to which coke dust is added, The zinc contents of the charge amount to 52 to 54 per cent., a lean coal being used as the reducing agent, and its weight being 40 per cent. of that of the calcined ore. The time required for distillation, including that of charging, is 24 hours. Each block will treat some 8 tons of calcined ore in this time, with a consumption of 8·5 to 9·2 tons of coal as fuel. For 1 ton of zinc about 2·5 tons of coal are used for fuel and 1 ton for reduction. A muffle will last according to the quantity of iron and coke contained in the charge, from 40 to 50 days. A furnace block with 240 muffles requires 14 furnacemen, working for 8 hours, 2 firemen working for 12 hours, 2 lads working for 12 hours, and 1 labourer for wheeling ore, coal and residues.

Losses of Zinc in Treating Zinc Ores in Retorts and Muffles

As has been repeatedly stated, the losses of zinc in the process of distillation are very high compared to the losses in the extraction of other metals. They amount to 10 to 25 per cent. of the zinc contents of the ore, and only in very exceptional cases fall below 10 per cent. In the Rhine Provinces, Westphalia and Belgium, where ores averaging 45 per cent. of zinc are treated in retorts and small muffles, the losses average some 12 per cent. of the zinc contents of the ore. In Upper Silesia, where ores containing 20 per cent. of zinc are worked in large muffles, they amount to 25 per cent. of the zinc contents of the ore. In Freiberg, where blende containing 30 to 31 per cent. of zinc is worked in small Silesian muffles, they amount to 18 per cent. The loss of zinc at the works of the Vieille Montagne at Angleur, in Belgium, amounts to 10 per cent.; at the Bleyberg works, in Belgium, to 13 to 14 per cent.; at Münsterbusch, near Stolberg, to 10 per cent.; at Bergisch-Gladbach to 10 to 13 per cent.; at the Wilhelmina Works in Upper Silesia to 21 per cent.; and at many other works in that district to 25 per cent. These losses are due to the passage of zinc into the material of which the retorts consist, the escape of zinc through the pores of the retorts, and through cracks in the retorts, or from the retort breaking completely, through the escape of uncondensed zinc out of the adapters, through zinc remaining behind in the retort residues, and through the escape of zinc vapours when the residues are being removed from the retorts. Retorts newly introduced into the furnace only give their normal output of zinc after the lapse of several days, because their walls absorb a certain quantity of zinc at first. This metal combines with the clay of the retort to form an aluminate—an artificial zinc spinel. This compound gives the material of the retorts the well-known blue colour. The average zinc contents of old retorts, no longer fit for use, amounts to 6 per cent. It may, however, as has been shown at the Bethlehem Works in Pennsylvania, rise to 21 per cent. By the addition of coke to the material of which the retorts are made, and to their manufacture under heavy pressure, the absorption of zinc has been greatly reduced at the works on the Rhine and in Belgium. Retorts, especially when not made under heavy pressure, are porous and allow zinc vapour to escape through their pores owing to the pressure in the retort during the processes of distillation. These vapours escape into the furnace and pass away with the products of combustion. If the pressure in the retorts is low, and that of the burning gases inside the furnace high, these gases and air penetrate into the retorts through the walls of the latter, and exert an oxidising action upon the zinc vapours in consequence of the oxygen and carbon dioxide which they contain. In order to avoid these defects, the retorts have been glazed, but this method has been shown to be less effective than that of manufacturing retorts under hydraulic pressure. In fact, this method of manufacturing retorts must be looked upon as an important improvement in the direction of diminishing the losses of zinc due to the porosity of the retorts. Great losses of zinc are caused by the cracking or breaking of the retorts, as in these cases zinc vapours escape freely from the retorts into the furnace, and where regenerators are used, may cause the passages in the latter to be stopped up. The loss of zinc due to this cause is greater, the lower the durability of the retorts. Upon the average, retorts, as also both small and large muffles, last some 40 days. Out of 100 retorts in use, 2 are broken per diem at Angleur in Belgium; 3 in Ampsin in Belgium; 2 (small muffles) at Münsterbusch; 2·5 (large muffles) at Hohenlohe; 2·6 (large muffles) at the Silesia Works in Lipine. The fact that retorts and small muffles manufactured under pressure in Belgium and the Rhine districts are not more durable than the large ones made by hand in Silesia is due to the circumstance that retorts and small muffles are only supported at their two ends and have to resist a very intense heat. Nevertheless the durability of retorts and small muffles is increased markedly in consequence of this method of manufacture, seeing that their average life used formerly only to be 25 days. The loss of zinc due to the escape of its vapour from the adapter has been diminished to some extent by improvements in the latter, such as those of Kleemann, Dagner and Steger, but is still very considerable. The loss due to the escape of zinc vapour from the retorts whilst the residues are being removed from the latter has not been avoided up to the present. It is generally assumed that the loss due to volatilisation of zinc owing to the above causes, amounts to half of the total loss. The loss of zinc due to the remaining of metal in the distillation residues in the retorts is also very high, seeing that these contain 2 to 8 per cent. of zinc. This loss is greater, the less the zinc contents of the ore. In Upper Silesia, where the average proportion of zinc in the ore treated amounts to 20 per cent., the retort residues are not allowed to retain more than 3 to 4 per cent. of zinc; whilst in Belgium and the Rhine Provinces, where the ores average 45 per cent. of zinc, it may average 4 to 5 per cent. The zinc which enters the retorts in the form of sulphide is not reduced, and therefore increases the zinc contents of the residues. Dead roasting of zinc blende is therefore an indispensable condition for good working. In spite of the very high losses of zinc which still obtain, the advances that have been made towards their diminution deserve recognition; and it must not be forgotten that whilst in the Rhine Provinces, Belgium and Westphalia, where retorts and small muffles are used, treating ores with 45 per cent. of zinc, the loss of zinc with good working formerly amounted to 18 to 22 per cent., at present it does not exceed 12 to 13 per cent. On account of the poorer ore treated in Upper Silesia, the losses in that Province are naturally far higher than on the Rhine or in Belgium. If the zinc contents in the distillation residues be assumed as averaging 4 per cent., as is the case on the Rhine and in Silesia, the ores of the

Rhine containing 40 per cent. of zinc would thus lose 10 per cent., whilst in Upper Silesia, where the charge contains a minimum of 18 per cent., the loss would amount to 23 per cent.

Data for Calculating the Cost of the Distillation of Zinc

The costs of zinc distillation comprise the costs of fuel, clay, wages and repairs. Under the Belgian method, ores containing 50 per cent. of zinc are treated, and with a charge of 63 lbs. per retort 3 to 4 tons of coal are at present consumed per ton of zinc, whereas the consumption formerly amounted to 7 to 8 tons. The consumption of fireclay amounts to 4 cwts. per ton of zinc, including the clay required for retorts, adapters, firebricks and furnace repairs. One man is required per 24 hours to each 14 retorts, or 5·8 men to the ton of zinc. In the Belgo-Silesian process, with several tiers of small muffles one above the other, taking charges of 75 lbs. per muffle, in Belgium, the Rhine Provinces and Westphalia, ores with 40 to 50 per cent. of zinc consume the same amounts of coal and fireclay per ton of zinc as in the Belgian furnace. One man is required per 24 hours for 13·3 muffles, or 4·8 men to the ton of zinc. In the Belgo-Silesian process, with large muffles lying in one row, and taking charges of 227 lbs. each, the ores averaging 20 per cent. of zinc, the actual consumption of coal used per ton of zinc, including that required for reduction, amounts to 10 tons, of which 7 are consumed in heating. The consumption of clay is somewhat less than in Belgium and on the Rhine, being about 4 cwts. per ton. In 24 hours 1 man is required for every 13·6 muffles, or 4·5 men for 1 ton of zinc. With regard to the labour required about the furnaces of the various systems, it must be remembered that after the furnace has been emptied, cleaned and re-charged, which takes place once in 24 hours, it also requires firing, and wheeling in ore and coal, as also wheeling out the various products and residues. Emptying, cleaning, and re-charging the muffles of a furnace takes, for example, 6 to 8 hours for a Belgo-Silesian furnace, so that the working time of the actual furnacemen does not much exceed this period. A Belgo-Silesian furnace block, containing 200 to 240 retorts, would require, for example, per 24 hours, 12 to 14 furnacemen working 6 to 8 hours each; 2 firemen, 1 per 12 hours; 2 helpers, 1 per 12 hours; and 1 labourer for wheeling in and wheeling out various materials, working 12 hours. This makes 17 to 19 workmen for 240 retorts per 24 hours, or 1 man for 12·6 to 14 retorts. The conditions in Belgium and Upper Silesia are somewhat similar.

EXTRACTION OF ZINC FROM FURNACE PRODUCTS

The furnace products rich in zinc which form the object of zinc extraction are the following:—Zinc fume (*poussière*); zinciferous flue dust; residues from the adapters and distillation apparatus; so-called furnace calamine, or furnace accretions and deposits containing zinc, which form when lead, copper, silver and iron ores containing zinc are smelted; zinciferous skimmings, and calcined zinciferous silver ores. Among the bye-products may be named zinc-silver alloys, zinc-lead-silver alloys, and zinc-copper-lead-silver alloys. As a rule these substances, with the exception of the various alloys of zinc with lead and the noble metals, from which the zinc is obtained as a bye-product, are added to the charge during the zinc distillation, if necessary after undergoing suitable preparation. The above substances are but rarely treated by themselves in the retorts of zinc distillation furnaces, as a less pure zinc would thus be produced. Zinc fume is treated in some works in special furnaces for the extraction of zinc; zinc fume, or poussière, is pulverulent metallic zinc, which generally contains certain amounts—8 to 10 per cent.—of oxide of zinc, as also cadmium, arsenic, antimony, lead and other substances volatilised from the charge of the zinc distillation furnace. The zinc oxide mixed with it is due to the action of air and moisture upon the finely divided metallic zinc at the commencement of the process of distillation. This zinc fume is found in the adapters, nozzles and other condensing arrangements of the distillation furnace. It is generally added to the charge of the distillation furnace in such proportion that its impurities may be distributed over large quantities of zinc, and thus have a less injurious effect upon the properties of the metal. On account of its easy reducibility, it is treated in those vessels which are least exposed to the action of heat. If zinc fume is treated by itself in distillation furnaces, zinc of an inferior quality is obtained, which is either mixed in with larger quantities of pure zinc, or is sent into the market as zinc of an inferior quality. In this case the zinc fume is charged either into the less strongly heated vessels in the distillation furnace—that is to say, in the case of Silesian furnaces with several tiers of muffles into the lowermost muffles, or in the case of single Belgian furnaces into the topmost tier—or else it is treated when considerable quantities have accumulated by itself in ordinary distillation furnaces, the vessels in which, in this case, are charged for a certain time with zinc fume alone.

According to Massart,[1] at the works of the Nouvelle Montagne at

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[1] *Rev. Univers. des Mines*, vol. xxx., p. 201.

Engis, in Belgium, there were produced during a 38 day campaign of the distillation furnaces from 43 tons 16 cwts. of zinc fume, containing 81 per cent. of zinc, 33 tons 14½ cwts. of crude zinc, with a loss of zinc of 5 per cent., and a consumption of 3,220 cubic feet of coal for fuel, and 537 cubic feet for reduction. The furnace treated 24 cwts. of zinc fume and 14 cubic feet of coal in 24 hours. Before charging the furnace was cooled down to a dull red heat; during the distillation the fire was kept moderately low in order to prevent the charge from becoming pasty, as happens when the temperature is higher. The condensed zinc was removed 7 times per day from the adapters; in order to prevent zinc from running out from the adapters, the nozzles had to be removed from the latter, and they were plugged by means of clay. A special method of extracting zinc from zinc fume, which has, however, been given up at the present day at most zinc works, consists in melting the zinc out of the fume in the so-called Montefiore furnace. This can be done by pressing together at a moderately high temperature the separate fluid particles of zinc, when they unite to a fluid mass, only retaining small quantities of oxide of zinc, whilst the greater portion of the oxide is separated out. The melting is performed in furnaces containing two rows of vertical muffles made in the shape of a boot open at the toes. After the zinc fume has been charged, a clay piston attached to an iron rod is inserted into the leg of the boot. By the pressure of this piston upon the heated zinc fume, fluid zinc is expressed from it, and flows out through the openings at the toe of the boot. The construction of these furnaces, known as the Montefiore furnace, after their inventor, is shown in Figs. 140 and 141, in

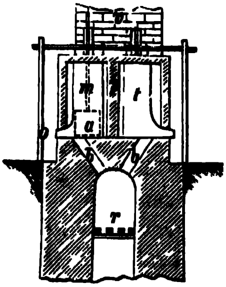

FIG 140

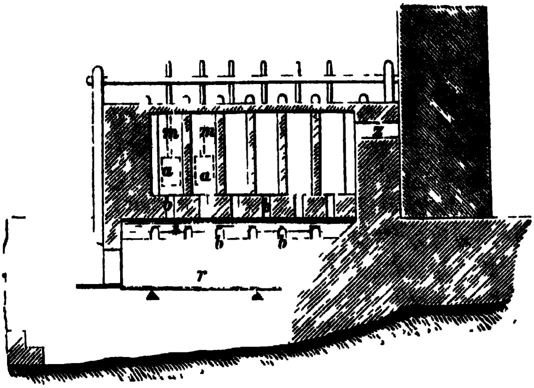

FIG. 141

which *t* are the clay boots, which are disposed in two rows in the interior of the furnace, and separated by the partition wall *s*. These boots are 28¾ inches high, 7·2 inches inside, and 9¼ inches outside diameter. The heating chamber is 6 feet 8 inches long, 3 feet 5 inches broad, and 28¾ inches high; *a* are the movable clay pistons 8¼ inches high and 6¾ inches in diameter, and *m* are the iron rods to which they are attached; *o* are the openings through which the zinc runs out or can be tapped out from the boots; *r* is the grate 5 feet 8 inches long and 18½ inches wide, from which the flame enters the furnace chamber through openings *b*, 3 inches wide, and after having surrounded the boots, escapes through the flue *z* into the stack *v*. At the Silesia Works in Upper Silesia a furnace was heated, not by a separate grate, but by the spare heat of the zinc distillation furnaces. The number of boots in a furnace varied from 8 to 12, there being 12 in the Figure shown above. The charge for a boot amounts to about 44 lbs. of zinc fume. After heating for 3 hours, the zinc will be in the fluid condition. Pressure is now applied, whereby the zinc is collected in the bottom of the boot and can be tapped out through the above-named openings. At Corphalie, in Belgium, a furnace of this kind treated from 14 to 18 cwts. of zinc fume in 12 hours, with a consumption of 116 to 155 cubic feet of fuel, and a zinc extraction equal to 85 to 86 per cent. At the Silesia Works, the output of zinc in Montefiore furnaces heated by waste heat amounted to 85 to 86 per cent. Zinc obtained from the Montefiore furnaces is exceedingly brittle in consequence of the amount of zinc oxide which it contains. For this reason the treatment of zinc fume in these furnaces has been given up in most works in favour of its treatment together with zinc ores in the distillation furnaces.

Zinciferous flue dust is also added to the charges. Should it, however, contain considerable quantities of lead, it may be treated with sulphuric acid in order to obtain the zinc in solution in the form of white vitriol, whilst the leady residue is smelted for lead.

The residues from the adapters of the distillation vessels as also the residues from the Montefiore furnaces, which consist essentially of zinc oxide, are either added to the charges in the ordinary distillation furnace, or else treated by themselves in the topmost tiers of retorts in Belgian furnaces.

The residues from the distillation vessels, retorts, or muffles contain 1 to 10 per cent. of zinc. In many cases they are submitted to a process of dressing, whereby a concentrate rich in zinc, a portion of unused reducing agent, and if the charge contains lead, lead also, are obtained; the enriched zinc concentrates are added to the charge for distillation.

Furnace calamine is also added in suitable proportions to the ore charge, after having been broken small.

Skimmings rich in zinc are treated in the same way, or are distilled together with zinc fume and the residues from adapters and vessels.

Calcined silver ores rich in zinc are treated in the same way as calcined zinc ores.

Alloys of zinc with lead and silver or gold are obtained when silver is extracted from work-lead by means of zinc. The zinc is recovered from these alloys by heating it to above the boiling point of zinc in retorts made of a mixture of clay and graphite, and by collecting the volatilised zinc in adapters. This method of zinc extraction has been fully explained under the head of the extraction of silver by means of zinc, Vol. i., p. 540.

Products of the Reduction Process

The products obtained in the processes of reduction are zinc, zinc fume, and residues from the adapters and distillation vessels.

Refining of Zinc

Zinc as raked or tapped out of adapters, or as removed in the form of solid zinc from the collecting chambers of the old Silesian furnaces, is but rarely pure. It generally contains considerable quantities of lead and iron, together with mechanically enclosed impurities. As these interfere with its extensibility, zinc which is intended for rolling must be freed as far as possible from these substances. This zinc, known as work-zinc or crude zinc, cannot be refined by an oxidising fusion, as is done in the case of silver, copper and lead, on account of the great affinity of zinc for oxygen. It may, however, be purified by slow remelting and allowing it to stand for a considerable time in the molten state. Under these circumstances the mechanically enclosed impurities which are lighter than zinc come to the surface, and can be removed as skimmings, together with a portion of the zinc oxide formed, whilst lead, as far as it is not alloyed with the zinc, and iron settle to the bottom in consequence of their higher specific gravities. The purified zinc can be ladled off from above the lowest portion of the bath of metal which contains the lead and iron, or this bottom part can be removed from the bath by means of an archimedean screw.

According to the temperature zinc will take up different quantities of lead; Roessler and Edelmann found that it will take up 5·6 per cent. at 650° C., whilst it takes up only 1·5 per cent. at its melting point. The latter amount cannot therefore be removed from the zinc by allowing it to settle. As most zinc ores contain lead, zinc containing a certain amount of lead will thus always be obtained in spite of refining. Work-zinc obtained in the solid state, as in the case of the old Silesian zinc furnaces, and as used to be the case with the English zinc furnaces, has to be remelted in order to cast it into moulds. During this remelting, which is performed in pans made of cast-iron or clay the impurities of the zinc separate out. To promote this operation, the molten zinc is stirred from time to time. The skimmings (zinc ash), which form upon the surface of the bath of metal, and which consist of a mixture of the separated mechanical impurities with oxide of zinc and metallic zinc, are removed by means of a perforated ladle. The zinc is finally cast into iron moulds, whilst the bottom portion of the metallic bath which is rich in lead, is ladled out separately. Cast-iron pans are open to the objection that they contaminate the zinc with iron, and thus make it brittle As a general rule, reverberatory furnaces with clay hearths should be used for the refining of zinc, as is done, for example, at the larger works of Upper Silesia, the zinc in which contains 1·75 to 2 5 per

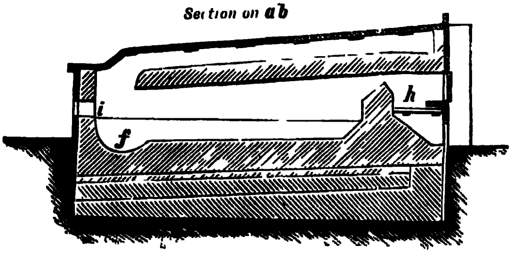

FIG 112

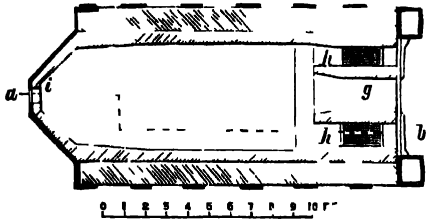

FIG 113

cent. of lead. The construction of such a furnace is shown in Figs. 142 and 143.[1] The inclined hollowed hearth is made of lean clay rammed upon the brickwork of the furnace, and terminates in a sump *f*; *g* is the charging door through which the zinc which is to be melted, is introduced into the furnace; *h*, *h* are the fire-grates; *i* is an opening through which the purified zinc is ladled out. The flame traverses the furnace longitudinally and rises above the sump, passing thence to the stack. The waste heat is generally utilised for warming the chambers in which the zinc that is to be rolled, is heated.

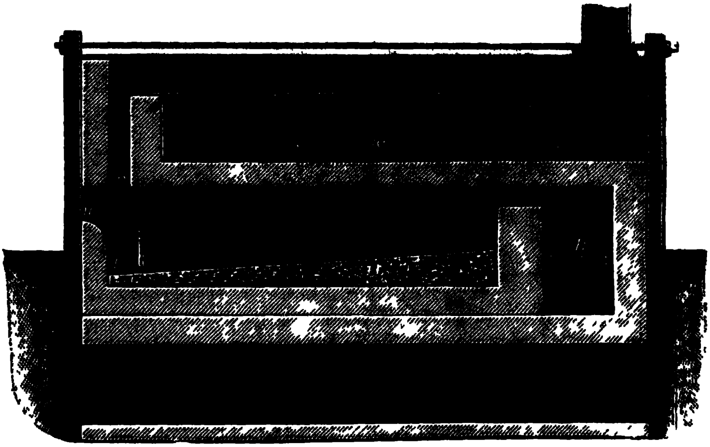

FIG. 144

Another form of furnace provided with only one grate is shown in Fig. 144. *R* is the grate, *s* is the bed of fire-clay, *t* is the sump, *u* is the door through which the metal is ladled out, *v* is the flue, *w* are chambers heated by the flame, in which zinc bars and sheets can be heated; *k* is a flue leading to the stack. At the flue end of the furnace there is a partition wall descending into the bath of metal in order to keep the air away from the latter. The opening for the introduction of the zinc into the furnace is at one side of the fire-bridge in a longer side of the furnace. The hearth is 15 feet 5 inches long and 6 feet 6 inches wide; the lowest point of the hearth is 1 foot 8 inches below the door out of which the metal is ladled. Such a furnace usually contains from 28 to 30 tons of zinc, and is capable of refining 9 to 10 tons in 24 hours, with a consumption of 18 cwts. of coal. A furnace similar to that first described, at the Hohenlohe Works, near Kattowitz, such as is used in most of the works in Upper Silesia, is shown in Figs. 145 to 147, 145 being a longitudinal section, 146 a horizontal section, and 147 a cross section of the furnace, the length of which is 19 feet 8 inches and its width 10 feet 6 inches; *r*, *r* are the two grates, between them is the flue *k*, inclining towards the hearth, in which the zinc to be refined is charged. From this it flows, as soon as it is melted, down the inclined surface of the hearth, to the sump *s*. The flame traverses the furnace lengthways from the grate and escapes through openings, *o*, in the roof of the furnace, into flues leading to the stack *E*. Such a furnace will contain 30 tons of zinc

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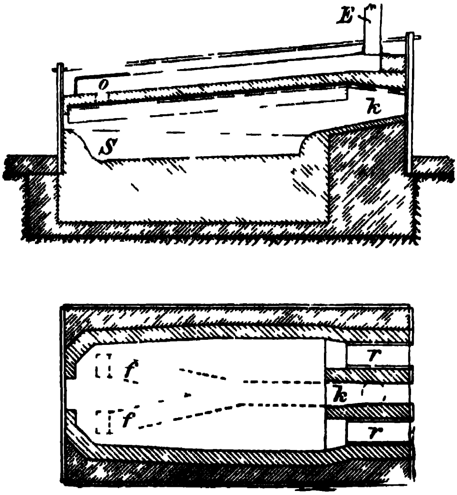
[1] *Berg. und Hütt. Ztg.*, 1873, p. 290.



Figs 145 and 146

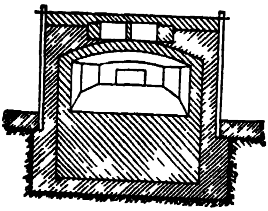


Fig 147

In order to avoid oxidation the zinc must be melted at the lowest possible temperature, and very gradually, whilst the flame is kept as reducing as possible. When the furnace has received its full charge of molten zinc—20 to 30 tons of zinc—which takes place after two or three days, the ladling out of the metal commences, as much fresh zinc being charged in as is ladled out, say 9 to 10 tons in 24 hours. From the metal bath, which is thus kept at a constant level, the lead first deposits, followed by the iron, which forms with the zinc and a portion of the lead a difficultly fusible alloy, whilst the zinc forms the topmost layer. By means of a suitable tool, the pure zinc, the hard zinc, and the lead are easily distinguishable from each other. If an iron rod is slowly lowered into the metallic bath in the furnace, the mass feels soft as far as the molten zinc extends; when the bar is forced further in, the mass feels hard, somewhat like ice at its melting point. This is the layer of hard zinc. Below this the soft layer of molten lead is reached. The mechanical impurities, which have a lower specific gravity than the zinc, separate out upon the surface. After the zinc has been skimmed, it is ladled out from the bath in cast-iron ladles made as thin as possible, and is cast into moulds in the form of bars; in this form it is known in the trade as *Spelter*. If the zinc is to be rolled, these bars must be kept heated up to 130° C. When properly worked, the quantity of skimmings does not exceed 1½ per cent. of the zinc charge. If the temperature is too high, a mixture of zinc oxide and fluid zinc known as *burnt zinc* forms upon the surface of the bath of metal. For the removal of antimony and arsenic from the zinc, L'hôte[1] proposes the addition of chloride of magnesium during the fusion, which is said to remove the above metals in the form of chlorides. Richards[2] recommends the addition of aluminium to the molten metal for the purpose of separating the impurities from the zinc. He claims that by this means the impurities, with the exception of lead, separate out at the surface.

From time to time, generally once a week, the bottom layer of zinc containing lead and iron, which has accumulated in the sump, must be removed from the latter. In this case, the whole of the zinc in the furnace is first ladled out, and then the impure bottom zinc removed, or else the bath of metal is left in the furnace and the zinc at the bottom is drawn out by means of a tube provided with an archimedean screw, or by means of an iron cylinder with a hole in the bottom, or again by means of an open clay tube, the bottom edge of which is notched, and which is inserted in the furnace before the commencement of the operation. The latter method allows the refining process to be carried on continuously, and is preferable to the two former. The first-named piece of apparatus consists of an iron tube or casing in which an archimedean spiral works. This tube is provided at its upper end with a spout through which the molten metal flows off, whilst the bottom end rests upon feet, the spiral being turned by means of a crank. The apparatus is inserted through openings, left for that purpose in the furnace, into the sump, and the handle is turned, whereupon the bottom layer of zinc rises in the tube and flows out through the spout; this apparatus is employed, for example, at Lipine. The second-named piece of apparatus consists of a cylinder with a hole in the bottom, this hole being plugged with clay. If the cylinder is lowered into the sump, and the hole in the bottom then opened, the impure zinc at the bottom rises into the interior of the cylinder and can be ladled out of it. The third piece of apparatus consists of a bottomless tube of fire-clay, the lower edge of which is notched. It is placed in the furnace before the leady zinc commences to separate, and is left in it during the whole course of the operations. The impure zinc passes into the tube through the notches and is ladled out from it as soon as it reaches a certain height. This apparatus is in use, for example, at the Paul and Wilhelmina Works in Upper Silesia.

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[1] *Comptes Rendus*, 98, p. 1491.

[2] American Patent, 448,802.

The consumption of coal in refining amounts to 7½ to 10 per cent. of the weight of the zinc melted. At Lipine, 9 tons of crude zinc, containing 2½ per cent. of lead, are melted in 24 hours, refined zinc with 0·75 per cent. of lead being produced. At the Hohenlohe Works 10 tons are melted in 24 hours, or 5 tons every 12 hours, containing 3 to 4 per cent. of lead, the refined zinc containing 98·87 per cent. of zinc, 1·07 per cent. of lead, 0·02 per cent of iron, and 0·04 per cent. of sulphur. The following table of analyses shows the impurities in the zinc (Spelter) produced at various works —

WORKS OF SOUTH WEST MISSOURI (ACCORDING TO PACK)

	I	II
Pb	0·0701	0·0061
Fe	0·7173	0·2863
As	0·0603	0·0590
Sb	0·0249	—
Cu	0·1123	0·0013
S	0·0035	0·0741
Si	0·0346	0·1374
C	0·1775	0·0016

	Lehigh, N J	Passaic, N J	Bethlehem, Pa
Zn	99·378	—	—
Cu	0·530	—	—
Pb	—	0·027	
Fe	0·041	0·020	0·0405
Cd	0·078	—	—
Si	—	—	0·2390

	Birkengang Works (Stolberg)	Cilli (Styria)	Johannisthal (Carniola)
Pb	1·460	0·3239	0·536
Fe	0·022	0·0253	0·018
Cd	—	—	0·069

	Georg Works, (Upper Silesia)		Recke works (Upper Silesia)	Sagor Works, (Austria)	
	I	II		I	II
Pb	1·4483	1·7772	1·1921	0·633	0·541
Fe	0·0280	0·0280	0·0238	0·032	0·010
Cd	0·0245	—	—	0·054	—
Cu	0·0002	—	0·0002	trace	
Ag	0·0017	trace	0·0007	trace	—
Sb	—	trace	trace	—	trace
Bi	—	—	trace	—	—
S	trace	0·0020	trace	trace	—

The purest zinc is what is known as Bertha spelter, produced at Pulaski, Va., from ores containing 47·61 per cent. of oxide of zinc, 29·37 per cent. of silica, 9·23 per cent. of ferric oxide and alumina, 4·54 per cent. of calcium carbonate, 2·7 per cent. of magnesium carbonate, and 8·23 per cent. of water. The zinc produced contains 99·981 per cent. of zinc, 0·019 per cent. of iron, and a trace of lead and silver.[1]

The impure bottom zinc, produced in refining, which contains considerable quantities of lead and iron is submitted either to distillation or to electrolysis, or else it is sold to silver works for the extraction of silver from argentiferous lead.

Skimmings rich in zinc, known as *zinc ashes*, are added to the charge in the processes of zinc distillation. A considerable portion of zinc, up to 60 per cent., can be liquated out from this substance by dusting salammoniac over it before it is drawn out from the furnace, or by heating it in a reverberatory furnace, after the zinc has been removed, and stirring salammoniac into it, ¼ pound of the latter being used to 100 pounds of zinc ash.

Zinc fume, *poussière*, contains the various volatile substances that are present in the charge for zinc distillation. The proportion of zinc oxide varies within very wide limits according as the zinc vapours have been burnt or not, or according as the zinc fume has been exposed for a longer or a shorter time to the air, the latter having an oxidising influence upon finely divided metallic zinc. The following analyses show the composition of various kinds of zinc fume:—

	Borbeck at Essen.	Carondelet Works, (Missouri).
Zn	97·82	29·899
ZnO	—	57·740
Fe	0·16	2·052
Pb	0·23	trace
Cu	—	trace
Cd	0·08	—
As		0·321
Sb	—	0·372
S		0·026
Carbon	—	1·221
Insoluble residue	-	9·608

Zinc fume from the collecting flues of the Silesia works (Lipine):—[2]

ZnO . . . . 54·45 = Zn . . . . 43·72
CdO . . . . 3·62 = Cd . . . . . 3·17
PbO . . . 12·34 = Pb . . . . . . 11·50
SO_3 . . . . 3·85
Fe_2O_3 and residue . 25·72

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[1] Moxham, *Eng. Min. Journ.*, November 25, 1893.

[2] Kossmann, *Preus. Minist. Zeitschr.*, 1883, pp. 236, *et seq.*

	First zinc fume from the Theresia Works, Upper Silesia.[1]		Average zinc fume from the Silesia Works, Upper Silesia.[1]
Zn	80·00	=Zn 86·684	84·463
ZnO	8·324		4·888
Cd	1·651		2·654
Pb	2·018		4·276
Fe_3O_4	1·022		0·903
Al	0·200		
Mn	1·815		—
CaO	2·804		2·464
MgO	0·675		0·239
Residue	1·020		0·120
(Containing carbon	0·230)		—

Zinc fume deposited in the dust flues connected with Kleeman adapters at the works of V. Giesche, Upper Silesia:—[2]

ZnO	88·20	SO_3	4·12
CdO	1·46	Mn_3O_4	0·05
PbO	4·44	Fe_2O_3 and residue	1·50

Dust deposited by water-spray in the flues, towers and chambers leading from a Dagner adapter:—

ZnO	66—94 per cent.
CdO	1·68—7·11
PbO	3·70—4·29
Fe_2O_3	0·50—3·87
Sand	1·16—3·45

The treatment of zinc fume has been explained on page 174. If it contains cadmium in workable proportion, it is used for the extraction of this metal. It is also employed, under the name of zinc gray, as a paint, especially for iron. Finally, it is employed as a reducing agent for the reduction of such substances as indigo, nitrobenzol and nitric acid in chemical factories and laboratories. It is also used for the preparation of hydrogen by heating it with slacked lime. The chemical change that takes place is said to be the following:—[3]

$$Zn + CaH_2O_2 = ZnO + CaO + H_2.$$

The residues from the adapters are treated as above mentioned. The residues from the vessels used for distillation are treated as mentioned above on page 176, if they are sufficiently rich in zinc, otherwise they are thrown away. In many cases they are used for road metal or in the preparation of mortar.

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[1] Kosmann, *Preuss. Minist. Zeitschr.*, 1883, pp. 234 *et seq.*

[2] Steger, *Zeitsch. d. Oberschles. Berg. und Hütt. Ver.* 1885, p. 222.

[3] Schwarz, *Ber. d. Deutsch. Chem. Gesel.*, 1886, 19,1140.

EXPERIMENTS AND PROPOSALS FOR THE IMPROVEMENT OF THE DRY METHOD OF ZINC EXTRACTION

Extraction of Zinc in Shaft Furnaces

Owing to the many shortcomings of the present method of zinc extraction, attempts have long been made to replace the process of distillation in clay vessels by distillation in shaft furnaces These attempts have, however, been fruitless as regards the production of solid zinc. It would be useless to fully describe the various methods and proposals which have been made in this direction, as, for example, those of Dyar, Rochaz, Shear, Duclos, Schmelzer, Swindell, Broomann, Lesoinne, Adrien,[1] Muller and Lancauchez,[1] Gillon,[2] Clerc,[3] Kleemann,[4] Keil,[5] Westmann[6] and Glaser.[7]

The whole of these have failed on account of the difficulty of condensing the vapours, as has been shown by the most recent exhaustive experiments carried out by Hempel.[8] Zinc vapours, which are mixed with considerable quantities of neutral gases, cannot be condensed by cooling to fluid zinc, because the zinc separates in a pulverulent condition. When shaft furnaces are employed for the production of zinc, the products of combustion, carbon monoxide and nitrogen, are necessarily mixed with the carbon monoxide produced by the reduction of oxide of zinc and with the zinc vapours. These latter are therefore diluted to such a degree that, when cooled, they will no longer condense to a fluid, but remain in the form of a fine dust suspended in the gases. Even when strongly heated air is employed for burning the coke in shaft furnaces, no change is produced in the behaviour of the zinc vapours, as has been shown by Hempel. In the present condition of science and technology, all attempts at the production of zinc in shaft furnaces must therefore be looked upon as presenting no probability of success. Pulverulent zinc readily oxidises in contact with the air, and therefore always contains certain quantities of oxide of zinc, as is the case with the above described zinc fume. Moreover, the oxidation of a portion of the zinc by the carbon dioxide and water vapours present in the furnace is also inevitable. By the employment of excess of fuel, by taking care that the charges and fuels shall contain neither water nor carbon dioxide, by the employment of ores which are free from oxide of iron (the latter being reduced already in the upper half of the furnace by carbon monoxide, and thus producing carbon dioxide), and by the employment of heated air, these objections can nevertheless be considerably limited, as is, indeed, also the case in the process of zinc distillation in smaller vessels.

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[1] *Berg. und Hütt. Ztg.*, 1862, p. 324.

[2] *Ibid.*, 1881, p. 6.

[3] *Ibid.*, 1887, p. 83.

[4] D. R. Patent, No. 14,497.

[5] *Ibid.*, No. 15,922.

[6] *Ibid.*, No. 19,127.

[7] *Ibid.*, No. 48,449.

[8] *Berg. und Hutt. Ztg.*, 1893, Nos. 41 and 42[2]

Whilst it is thus impossible to produce solid zinc in shaft furnaces, it is nevertheless quite possible, as Hempel has shown, to produce zinc oxide in such a furnace and also pulverulent zinc containing only relatively small quantities of oxide. The shaft furnace therefore presents a means for producing bye-products rich in zinc for distillation in retorts. In this respect, especially as regards the formation of pulverulent zinc, it may be worth while to experiment further upon the shaft furnace. According to Hempel's experiments, by the use of hot blast it is possible to obtain zinc fume very rich in zinc in the shaft furnace, and to separate it by means of centrifugal machinery from the gases. This zinc fume can be compressed into a very small volume by pressure, and this protects it from oxidation; from the zinc dust so treated zinc can be obtained both by distillation, without the addition of carbon, as also by means of electrolysis. Hempel submitted the compressed zinc dust to distillation, without adding carbonaceous matter, and obtained two-thirds of the fume in the form of metallic zinc of great purity. The residue contained oxide of zinc together with lead, silver, copper, &c., combined with oxygen and sulphur, which had been volatilised, together with the zinc, in the shaft furnace. Hempel used *zinc-coke* for the shaft furnace charge, this material being produced by heating together 1 part of zinc oxide, 3 parts of coal, and 0·05 part of caustic lime in a retort, and allowing the caked mass to cool with the exclusion of air. The shaft furnace was provided with an iron stove for heating the blast, and was constructed like a Sefstrom furnace. The gases, together with the zinc vapours, passed from the throat of the blast furnace into an iron tube, in which they were cooled down to 30° C. The gases were drawn off from the furnace and the zinc fume separated from them by means of a centrifugal apparatus, the construction of which is shown in Figs. 148 and 149. It consists of a wheel, *A*, with 8 vanes, which is driven by means of the grooved pulley, *a*, driven by a steam engine, the velocity being from 1,000 to 3,000 revolutions per minute. The wheel rotates inside a casing, *B*, which is again contained in the larger cylinder, *C*. The casing was open below, but closed above. The cylinder, *C*, was closed below by means of a cone, and provided above with a removable cover, *b*. The gases and zinc vapour entered through the tube *c*; when it reached the interior of the machine, the dust was flung, by centrifugal action, against the projections of the casing *B*, whence it dropped down into the conical portion of the cylinder *C*, where it was deposited and whence it could be removed by means of the spout *e*. The gases escaped through the tube *d*, and were made to traverse a bag in which the remainder of the zinc dust was retained, so that the gases escaping therefrom were perfectly free from fume. The proportion of carbon dioxide in the escaping gases, which, as is well known, decreases as the furnace temperature increases, and which amounts to under 1 per cent. at a white heat, had gone down to 0·7 per cent. before charging the zinc-coke furnace, and varied during the three hours that distillation lasted, between 1·8 and 4 per cent. of the gaseous mixture.

The zinc fume produced contained 72 to 90 per cent of zinc. It is liable to oxidise rapidly in the air, and if charged in the pulverulent form into retorts or muffles for the purpose of distillation, would require the addition of carbon for the reduction of the zinc oxide, together with a very high temperature. In order to avoid this oxidation, it was compressed into blocks. According to the experiments of Hartig,[1] a pressure of 30 atmospheres reduced it to 13·3 per cent. of its original volume, 100 atmospheres to 10 per cent., and 200 atmospheres to 8·7 per cent. Accordingly, as a pressure of 100 atmospheres can easily be produced by means of screws, levers or hydraulic presses, there is no difficulty in compressing zinc fume to one-tenth of its original volume. Hempel obtained, by the distillation of this compressed zinc by itself, without any addition of carbon, two-thirds of the weight of the former in the form of very pure metallic zinc. In treating a charge to which ferric oxide and

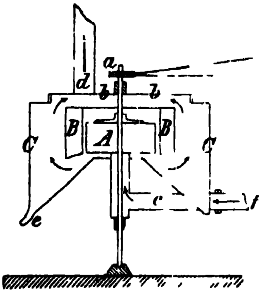

FIG. 118

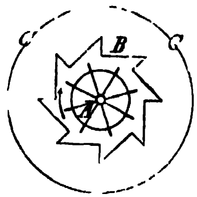

FIG. 149.

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[1] *Loc. cit.*

argentiferous lead had been added, Hempel obtained zinc fume containing 80 per cent. of zinc, which contained the whole of the lead and silver. The iron was obtained in the form of white pig-iron; the slag left in the furnace contained 58·3 per cent. of silica, 10·4 per cent. of alumina, 8 per cent. of ferric oxide, 15 per cent. of lime, 1·0 per cent. of zinc and 1·8 per cent. of sulphur. This zinc dust was also compressed and distilled without any addition of carbonaceous matter. Two-thirds of its weight were obtained in the form of pure zinc, together with a residue having the following composition:—

SiO_2	41·6	Zn	33·6
Fe_2O_3	2·93	S	8·1
CaO	0·6	PbS and Ag_2S	1·05

No experiments have been published with respect to the electrolysis of compressed zinc. It could be moulded into soluble anodes, and as the zinc is chiefly present in the metallic form, a considerable quantity of electrical energy would be developed by its solution, so that only a low current tension would be required. In consequence of the above experiments Hempel proposed the extraction of zinc from ores which contained considerable quantities of zinc in addition to lead and silver, and which cannot be separated by dressing operations into zinc ores on the one hand and lead and silver ores on the other. The process is to comprise the following operations:—

1. The production of zinc fume in shaft furnaces.
2. The compression of the zinc fume produced.
3. The distillation or electrical refining of the compressed zinc fume.

The ore, after having first been calcined, has to be fritted, or, if coking coal is available, ground, without being fritted, with this coal, and then coked. If the ore is rich in iron, the iron must first be reduced, otherwise zinc vapours would be re-oxidised by the carbon dioxide produced in the upper part of the furnace, as occurs in iron blast-furnaces. The gases evolved from the furnaces, after having been freed from the zinc vapour, consist essentially of carbon monoxide and nitrogen, and are to be used for heating the blast or the distillation furnace, and for firing boilers. On escaping from the furnace, the gases are first passed into iron tubes kept cool by exposure to the air, in which the former are to be cooled down to 50° C., and simultaneously to deposit a portion of zinc fume; they then enter one, or a series of, centrifugal machines, which they traverse one after the other, in which nearly the whole of the zinc fume still retained is separated out. Hempel proposes the centrifugal machines shown in Figs. 150 to 151. *A* is the fan, *B* the casing, *C* the cylinder. The fan is driven from below. It would be best, as is customary with centrifugal machines, to support the fan in a movable bearing with an india-rubber ring. If the speed of the fan for the separation of all the fume is found to be too high, it might be necessary to follow these machines by filters of sacking to separate out the last trace of zinc fume.

In order to avoid the formation of zinc oxide, the furnace should be so worked that the proportion of carbon dioxide in the escaping gases should not exceed 4 per cent. The compression of the zinc fume is to be performed in two operations. The first pressure is to be applied by means of a machine in which a spindle with a rapid pitch screw is quickly employed, so as to produce a pressure of 10 to 20 atmospheres, the final pressure being given by means of a hydraulic press. The distillation of the zinc dust, moulded into the form of cylinders, is to be carried out in retorts which are a trifle larger than the cylinders of zinc fume. Although these proposals of Hempel have not yet been carried out on a large scale, and practical results are therefore not available, they nevertheless deserve full consideration. With ores carrying considerable quantities of lead and silver, difficulties may be met with in practice, as, on the one hand, fluid argentiferous lead and a considerable quantity of slag rich in zinc would be formed in the blast furnace, whilst, on the other hand, the zinc fume obtained would contain considerable quantities of lead, the treatment of which in retorts presents difficulties.

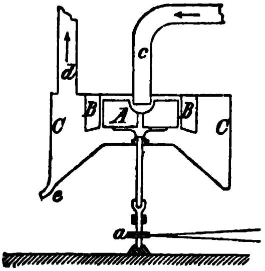

FIG. 150

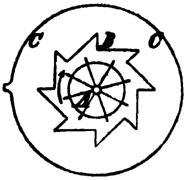

FIG. 151.

The production of zinc oxide, or of a mixture of zinc and zinc oxide, in shaft furnaces presents no technical difficulties, if the formation of carbon dioxide by the combustion of the fuel is favoured by blowing an excess of air into the furnace, and, generally speaking, if an excess of air is present in the furnace. In the case of charges rich in iron, the formation of carbon dioxide is promoted by the fact that ferric oxide is reduced to metallic iron at a low red heat by carbon monoxide with the formation of carbon dioxide. In these cases, the zinc would be reduced in the lower part of the furnace by means of the carbon present. The excess of air, together with the carbon dioxide present in the upper part of the furnace, would again oxidise the vapours of zinc as they rise up. This takes place, for example when ores of iron, lead, copper or silver, containing zinc, are smelted in furnaces of comparatively small height. That the reduction of zinc takes place without any difficulty in these cases, is proved by the method to be presently explained for the production of zinc white direct from the ores. It is necessary to cool down the zinc fume and to separate it from the neutral gases by means of dust chambers and filtering appliances. Of the shaft furnaces that have been patented for the production of zinc oxide, not a single one, as far as the author knows, has been used practically. Zinc oxide intended for reduction has, up to the present, only been obtained as a bye-product when zinciferous ores such as franklinite are smelted in shaft furnaces, or when zinc white is produced in furnaces with Wetherill grates (see the production of zinc white).

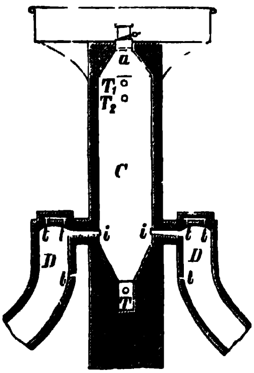

Fig 152.

As an example of a patented shaft furnace for the extraction of zinc oxide from ores, the furnace of Harmet may be mentioned, although it also has not been used practically.[1] The furnace, Fig. 152, has a closed top, *a*; by means of tuyeres, T^1, T^2, in the upper part of the furnace, as also by means of the tuyeres *T*, situated just above the bottom of the furnace, hot air is forced into the latter. The zinc reduced from the ores escapes in the form of vapour through the flues, *i*, into the chambers, *D*, where it is completely oxidised by means of cold and moist air entering through the tubes, *t*, and is then to be collected in the form of zinc oxide in chambers. The residue, free from zinc, is to be fused into a slag in front of the tuyere *T* and to run out of the furnace. For the production of metallic zinc, which is, however, subject to the above-named difficulties, the furnace is to be made higher. In this case, the zinc vapours are to be conducted, at a certain pressure which prevents the entrance of atmospheric air, through chambers filled with charcoal, and then passed into condensers. For the above-named reasons, here also zinc fume alone would be obtained. For the production of zinc oxide, furnaces with Wetherill grates are better suited than are shaft furnaces.

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[1] D. R. Patent, No. 11,197.

Biewend has recently proposed the blast furnace for the decomposition of zinc blende by means of iron.[1] The iron is to be added either in the metallic state or reduced from oxides charged for that purpose. The fuel and reducing agent for the oxide of iron is to be coke or charcoal. The zinc separated out in the gaseous form is to be conducted at a high temperature—800° C.—into condensers filled with red-hot coke or charcoal and condensed therein to the liquid state, whilst the sulphide of iron formed by the decomposition of the sulphide of zinc, and the slags produced from the ashes of the fuel and the impurities of the zinc blende, forming a silicate of lime and alumina, are to be tapped out of the furnace in the molten condition. The sulphide of iron can be converted into ferric oxide by calcination, and after being reduced can be used for the decomposition of fresh quantities of sulphide of zinc. The gases, freed from zinc in the condensers, and which consist of nitrogen and carbon monoxide, are to be used as fuel. The possibility of the decomposition of sulphide of zinc by iron in blast furnaces has been proved by the smelting of iron ores containing zinc blende. As, however, the zinc vapours formed are also diluted in this case by vapours of nitrogen and carbon monoxide, it is doubtful whether the zinc can be condensed to a liquid even by the employment of condensers filled with red-hot coal. That the condensation of zinc to a liquid may be possible to a certain degree, has been proved by the production of fluid zinc in the so-called *zink stuhl*, in the old shaft furnaces of the lower Hartz, in which zinciferous lead ores were formerly smelted. If the condensation of zinc in the liquid state is not feasible, it would be necessary to be content with the production of rich bye-products. Hitherto no experiments have been tried on a large scale upon this process.

The Extraction of Zinc in Reverberatory Furnaces

The extraction of zinc in reverberatory furnaces has been attempted, but has always been attended with unfavourable results. In consequence of the oxidising action of the gases in these furnaces, zinc oxide was always obtained, but never the metal. Brackelsberg[2] attempts to avoid the oxidation of zinc by moulding a mixture of ground ore and coal into bricks, which he builds into columns in the laboratory chambers of reverberatory furnaces heated by producer gas, filling the interspaces between these columns by briquettes of coal or other carbonaceous fuel. The producer gas is to be burned by means of air introduced either by pressure or by draught. The flames are to pass through vertical spaces, left when the briquettes are built up, from above downwards, into a condensing chamber built below the laboratory chamber of the furnace, and thence into the gas producer of a second furnace. By means of the flames, these briquettes are to be heated to the temperature of reduction of the zinc, the excess of carbon in the furnace reducing the carbon dioxide to carbon monoxide. In the condensing chamber blocks of metal cooled by water and covered with fireclay are distributed. The zinc is supposed to collect in the liquid form upon the bottom of this condenser and to be tapped off from time to time. Nothing is known up to the present as to the employment in practice of this furnace. Even though it might be possible to avoid the oxidation of the zinc, the zinc vapours would be diluted to a very great extent by the products of combustion of the producer gas and the nitrogen of the air, so that it would be impossible to count upon the production of liquid zinc. As in the case of the shaft furnace, zinc fume would be formed; the production of liquid zinc in reverberatory furnaces must therefore be looked upon as hopeless, as only bye-products rich in zinc could be obtained in them.

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[1] D. R. Patent, No. 81,358, August 7, 1894.

[2] D. R. Patent, August 27, 1893.

Proposals for the Improvement of the Condensation of Zinc Vapours when the Distillation Process is carried on in Vessels

As is well known, in the present method of zinc extraction the condensation of the vapours is the weakest point of the process. The greater part of the loss of zinc is due to the fact that a portion of the zinc vapours is never condensed at all, and that another portion, on account of its low tension as compared with atmospheric air, is not expelled from the retorts, but burns when the latter are emptied out. The condensation of zinc vapours is only perfect between the narrow temperature limits of 415° and 550° C. If the temperature of the adapter, in which condensation takes place, is lower than 415°, the zinc passes from the condition of vapour direct to the solid state and forms a fine dust, which is in part carried of by the neutral gases. If the temperature exceeds 550° C., the zinc vapours escape without being condensed. Imperfect condensation is due to the impossibility of regulating the temperature of the small adapters at present in use, which, in consequence of their close connection with the furnace, necessarily fluctuates with every variation in the temperature of the furnace. Zinc vapours remain in the retorts at the end of the distillation, because on account of the present method of connecting retorts and adapters it is impossible to draw these vapours out of the retorts into the adapters by means of draught.

L. Lynen, of London,[1] has constructed a condensing chamber common to several adapters, which is to replace the present form of condenser and to avoid the above-named objections. Its arrangement is shown in Figs. 153 to 155. There are here two condensing chambers, *b*, about which four separate furnaces, separately fired, are so arranged that one condensing chamber lies between each pair of furnaces. The furnaces are fired with gas, and have three tiers of muffles, *a*, one above the other. These are luted to perforated bricks, *d*, which are so shaped that they connect the common condensing chamber with the back end of the muffle. The con-

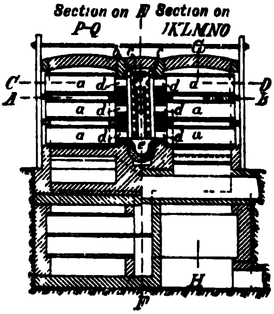

FIG. 153.

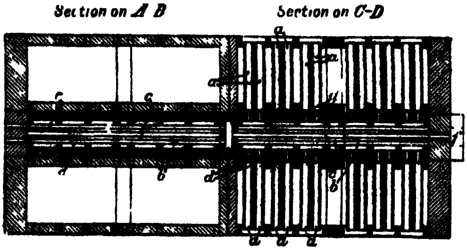

FIG. 154.

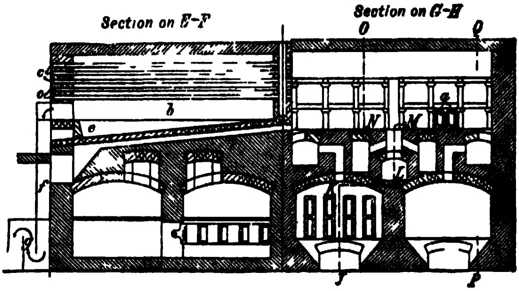

FIG. 155.

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[1] *Zinc Distillation with a Common Condensing Chamber*, L. Lynen. London, 1893; August Siegle, 30, Lime Street.

denser has a sump, *e*, from which the zinc can be tapped off, and a bath of zinc of a definite depth is always left in the condenser to regulate the temperature. For the same purpose, there is a row of tubes, *c*, through which air can be admitted into the condenser and thus cool it if required. It is connected by means of the flue *f* with the dust flues *g*, and with a dust chamber in which any zinc fume formed is collected. From this dust chamber the current of gases passes into a stack connected with it. In consequence of the connection of retorts, condenser, dust chamber and stack, it is possible to draw any zinc vapour that may be left in the retort at the end of the distillation out of that retort by means of a light draught. The thickness of the walls of the condenser, the bath of zinc at the bottom, and the passage of air through the air tubes in case the condenser becomes overheated, are supposed to make it possible to keep the temperature of the condenser within the requisite limits. The bath of zinc not only acts as a regulator, but promotes condensation by surface attraction. Finally, it also admits of the lead separating out in the lower portion of the sump and thus forms a partial refining furnace. When the distillation is finished, the system is to be worked with a gentle draught in order to draw out the last traces of zinc vapour from the retorts; as in this case air has to be admitted into the retorts, it is possible that a portion of the zinc vapours may be converted into fume. These proposals of Lynen would seem to deserve consideration, although nothing is known up to the present of any practical results obtained from them.

Proposals for Improving the Material and Shape of the Vessels

Steger[1] has proposed to replace clay, on account of its many defects, by magnesia and to build fixed muffles from tiles made of this material, which are to be much larger than the vessels at present employed for zinc distillation. According to his statements, magnesia conducts heat 2½ to 3 times as well as clay, is impenetrable by zinc vapours, is much stronger than clay, and resists higher temperatures. The construction of the furnace as proposed by Steger in the above-named treatise is shown in Figs. 156 and 157, the first a longitudinal and the second a transverse section of the furnace; *a* are three retorts built of magnesia bricks with arched roof and floor. Between the separate retorts there are flues *d*, in which the producer gases are burnt by means of heated air, these gases being led by means of slots from the shafts *c*, into the flues *d*. The air for combustion is heated in the retort *W*, and then enters the flues *d*. The products of combustion escape through slots into the vertical flue *e*, pass at the upper end thereof into the flue *f*, and finally through *g* to the stack. Hereby the bottom as well as the top of the muffles are completely surrounded by the flame. The retorts are charged and emptied at their back ends where they open out into a vertical flue, *p*. The gases and vapours which escape during the charging and drawing rise up in this flue, whilst the distillation residues fall downwards. The adapters, *i*, are at the front ends of the retorts in a vertical chamber, *h*, to the back-wall of which the retorts are secured air-tight There are no statements regarding the dimensions of the retorts. Their size and thickness are to be calculated from the conductivity of the magnesia, from the heating capacity of the gas flues, and from the conductivity of the material of the charge. The advantages of the magnesia vessels which are chiefly dwelt upon by Steger, are their great durability, the small loss of zinc during the operation, the possibility of charging them with ore in the finest state of division, the non-existence of any necessity for replacing retorts, greater durability of the adapters, and larger dimensions of the latter, more rapid charging and drawing, and easier and more healthy work. With respect to the durability of these magnesia vessels, Steger is of opinion that they would last for several years, whilst clay muffles and retorts, on the other hand, only last on the average some 40 days. Steger's furnace has been patented in the name of his partner, Francisci, in Schweidnitz.[1] Experiments with this furnace are now being tried in Silesia. The magnesia bricks at first used showed themselves to be very sensitive

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[1] *Preuss. Minis. Ztschr.*, 1894, p. 163.

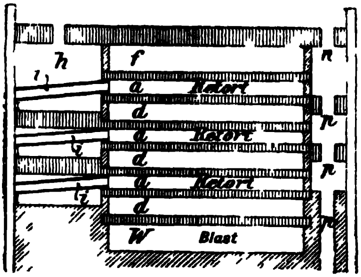

Fig. 156

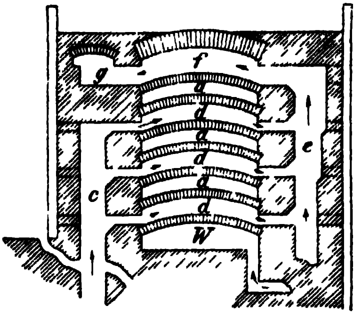

Fig. 157

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[1] D R. Patent, 76,285; Belgian Patent, 107,606; British Patent, No. 23,979; Austrian Patent, 44/3256; American Patent, 526,808.

to changes of temperature. According to communications from Dr. Steger, this difficulty is said to have been overcome at present. No conclusive opinion can be formed of the furnaces until they have been in work for some considerable time, which has not been the case up to the present.

THE EXTRACTION OF ZINC BY THE COMBINED WET AND DRY METHODS

The direct extraction of zinc by the wet method is not possible because zinc cannot be thrown down in the metallic form from its solution by any metals that are permanent at ordinary temperatures. Apart from the separation of this metal by electrolysis, only compounds of zinc can be produced in the wet way, from which the zinc must be reduced in the dry way. The wet method of zinc extraction can therefore only be looked upon as an auxiliary process for the dry method, in which the zinc is obtained from ores and metallurgical products in the form of aqueous solutions, from which compounds of zinc can be obtained that can be converted into oxide. The reduction of the oxide to metallic zinc is performed in the dry way. The combined wet and dry way of zinc extraction has, however, up to the present been found to be too dear for practical purposes. Zinc has been extracted from poor ores and furnace products by means of sulphuric acid, hydrochloric acid, ammonia, ammonium carbonate, magnesium chloride, calcium chloride, carnallite, and by a chloridising roasting followed by leaching of the chloride of zinc so formed, the products being solutions of zinc sulphate, zinc chloride, ammonio-zincic hydrate, and ammonio-zincic carbonate respectively. Zinc oxide has been produced from the solution of the sulphate by evaporating the latter and heating the zinc sulphate obtained, sulphuric anhydride and sulphurous oxide and oxygen being given off. The process has not, however, been employed upon a large scale.

Parnell proposes[1] to obtain zinc sulphate by treating calcined ores containing zinc oxide with sulphuric acid, to evaporate the sulphate solution until it commences to thicken, then to stir sulphide of zinc into the mass, and to heat the mixture in a muffle furnace. Sulphur dioxide, which is to be used for the manufacture of sulphuric acid, is said to escape while zinc oxide is formed, in accordance with the equation:—

$$3ZnSO_4 + ZnS = 4ZnO + 4SO_2$$

This reaction is probably very imperfect, as it is not possible to convert the whole of the zinc into zinc oxide. This proposal has not, therefore, found any employment.

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[1] *Karnthner Ztschr.*, 1881, p. 32.

W. Marsh has proposed to precipitate zinc hydrate from a solution of the sulphate by means of magnesia. On account of the high cost of magnesia, this process cannot be employed upon a large scale. By heating zinc sulphate with carbon upon a large scale, zinc oxide is only incompletely formed.

Zinc chloride can be obtained by the treatment of bodies containing the oxide or carbonate of zinc with hydrochloric acid, magnesic or calcic chloride, or with carnallite, or by the calcination of zinc blende with common salt; and zinc oxide can be obtained cheaply by treating the solutions so produced with milk of lime. In addition to zinc oxide or hydrate, zinc oxychloride is also formed, and this method for the production of zinc oxide has been found to be unsuitable for operations on a large scale.

Of the salts of ammonia, carbonates show the greatest capacity for dissolving zinc oxides from ores and products,[1] having considerably greater dissolving powers than has ammoniacal liquor. The most suitable solutions are those containing 7 to 8 per cent. of ammonia and 7 to 8 per cent. of carbon dioxide. By distilling off the ammonia and the greater part of the carbon dioxide, the zinc can be separated as a basic carbonate, whilst the solution is regenerated with the exception of a certain quantity of carbon dioxide which has to be replaced. The basic zinc carbonate can be converted into oxide by heating. This method is too expensive for the extraction of zinc from poor ores, and has therefore only been used for the extraction of zinc oxide from argentiferous metallurgical products.

Although, therefore, the combined wet and dry method of zinc extraction from poor ores has not yet passed the experimental stage for the reasons above stated, it has nevertheless come into use in those cases in which the object is not the extraction of metallic zinc, but the separation of zinc from other valuable metals and metallic compounds, and the conversion of the zinc into a bye-product in the form of merchantable compounds such as zinc vitriol, zinc chloride, basic zinc carbonate or zinc white, as also for the production of zinc salts from residual products containing zinc. Where and to what extent the wet method may in the future find employment as an auxiliary process to the dry way for the production of compounds rich in zinc from ores or artificial products poor in zinc cannot at the present day be decided. Stahl[2] has determined by a series of experiments to what extent the zinc contained in burnt pyrites can be converted into chloride by chloridising roasting, and what proportion of zinc volatilises in this process. The zinc is contained in the burnt ore as sulphide, sulphate and oxide. It was not found possible to convert the zinc in pyritic residues containing 7 to 11 per cent. of zinc completely into chloride by a single chloridising roasting even although pyrites was added, which greatly promoted the formation of sulphate. On the other hand, the chloridising of zinc was almost complete when the once roasted and then leached ores were submitted to a second chloridising roasting with the addition of pyrites. Only 2 to 3·5 per cent. of zinc volatilised during calcination in the form of zinc chloride, which was caught again in condensing towers.

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[1] Schnabel, *Preuss. Ztschr.*, vol. xxviii.

[2] *Berg. und Hütt. Ztg.*, 1894, p. 1.

THE ELECTROLYTIC EXTRACTION OF ZINC

The electrolytic extraction of zinc is quite modern. Up to the present the extraction of zinc in the wet way only has been the object of continuous energetic experiments, and, in fact, in some cases the process has been actually employed upon a working scale. The extraction of zinc in the dry way by the electrolysis of molten compounds of the metal has not yet been attempted on a working scale, although propositions in this direction are not wanting. We have first to consider the electrolytic extraction of zinc in the wet way, and then the proposals for its electrolytic extraction in the dry way.

The Electrolytic Extraction of Zinc in the Wet Way

As far as is known, experiments with this object were first made at the end of the seventies by Luckow in Deutz, and at the commencèment of the eighties by Letrange, of Paris, without their experiments leading to any satisfactory results. They were not able to obtain the zinc in compact fusible masses, but only in a spongy form, in which condition it cannot be melted, but burns at the temperature required for the fusion of zinc. This also happens even when the zinc sponge is first compressed, and then introduced into a bath of molten zinc. At the same time, the tension of the electric current required to decompose the electrolyte is a comparatively high one, namely, 2½ to 4 volts. Although there are still various opinions as to the reasons that cause the zinc to separate in the spongy form, continual experiments have at present attained the result that compact pure zinc can now be obtained by means of electrolysis on a large scale, and that this can readily be re-melted.

Up to the present, however, the extraction of zinc from zinc ores proper by electrolysis has not been employed on a working scale on account of the high costs due to the great waste of electric energy and to the necessity of employing special precautions for the production of a compact deposit. It has, however, been employed for the extraction of zinc from ores which do not contain it as their principal constituent and the value of which is increased by the removal of zinc from it, as, for instance, zinciferous pyrites residues, also for the parting of zinc from metals with which it is alloyed, and for the refining of zinc. Its employment may also be worth considering for the separation of zinciferous lead and silver ores, from which the zinc cannot be removed by dressing operations completely, nor without incurring considerable loss of both metals—especially of silver—as also for the removal of zinc from zinciferous silver ores.

It is perfectly possible that where cheap motive power—such as water-power—is available, this method might be employed for the treatment of zinc ores proper, especially if they contain an appreciable quantity of silver, which is not paid for by the zinc works.

Zinc separates in the form of sponge, both in neutral and feeble acid solutions, and when either soluble or insoluble anodes are employed. The causes of the sponginess have been variously assumed to be the molecular modification of zinc by hydrogen, by hydrogen and zinc hydride, the formation of zinc oxide, the presence of foreign metals in the electrolyte, and the formation of haloid acids and oxychlorides. Kiliani found, in the course of his experiments[1] to determine the conditions of the deposition of compact zinc from solutions of zinc vitriol, that, even when soluble anodes were employed, if the current tension was low, gas was evolved, and the zinc became spongy; but that, on the other hand, if the current tension was high and the solutions not too dilute, no gas was evolved, and the zinc was compact and brilliant. He also found that when highly dilute solutions were employed, hydrogen was actively evolved, and that the zinc was always spongy, whether the current was feeble or strong. With feeble currents, zinc oxide, together with zinc, was deposited from dilute solutions. For instance, from a solution containing 1 per cent., with a current tension of even 17 volts, oxide of zinc was deposited when only 0·0755 gram of zinc was thrown down per minute upon a 1 square centimetre of cathode area. The results of Kiliani's experiments are shown in the following table.[2] They refer to a solution of zinc vitriol of specific gravity 1·38, anodes and cathodes being made of sheet zinc:—

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[1] *Berg. und Hütt Ztg.*, 1883, p. 251.

[2] Borchers, *Elektro-Metallurgie.* Brunswick, 1891, p 96

Zinc deposited per minute per sq. centimetre of cathode surface	Ampères per square metre.	Gas evolved per 1·5 grams of zinc deposited	Nature of the deposit
Milligrams		Cub. cent	
0·0145	7	2·40	Very spongy.
0·0361	18	2·27	do.
0·0755	38	0·56	do.
0·3196	158	0·43	More compact, but spongy at the edges.
0·6392	316	0·33	Can still be wiped off readily.
3·7274	1,843	-	Firm and lustrous, with bud-like projections round the edges.
38·7750	19,181	—	

From a 10 per cent. solution, Kiliam obtained the best deposits when the current was equal to 0·4 to 0·2 milligramme of zinc. Hence it seems that excessively great current tensions, up to 171 ampères per square foot, are necessary to produce a compact deposit of zinc.

Nahnsen,[1] in his experiments to determine the most suitable current densities and temperatures for the deposition of compact zinc from solutions of zinc vitriol, found that hydrogen (primarily generated by the addition of sulphuric acid to the solution of zinc vitriol, plates of zinc being used as anodes), which formed in great quantity at the cathodes, does not make the zinc spongy, and therefore assumed that the sponginess was due entirely to the formation of zinc oxide. According to him, the hydrogen which appears at the cathode simultaneously with the spongy deposits, is of a secondary nature, produced by the action of the deposited zinc upon the water of the solution. Nahnsen further tried experiments upon the character of the zinc deposited at various tensions and temperatures. These were tried upon solutions of zinc sulphate whose specific gravities at 18° C. were respectively 1·0592, 1·1233, 1·1925, 1·2710, 1·3543, and 1·4460, using soluble anodes in the form of zinc plates of 0·054 square foot in area. The results obtained are shown in the following table, in which the density of the current, the temperature of the electrolyte, and the character of the deposit are indicated :—

Current Density.	Temperature of the Electrolyte.			
Ampères per sq. foot	+ 0·97 C.	+ 10·05° C.	+ 20·72° C	+ 30·47 C.
0·93	Compact	Spongy	Spongy	—
4·57	Compact	Spongy at first	Spongy	—
9·13	Compact	Compact	Spongy at first	Spongy
13·60	—	Compact	Compact	Spongy at first
18·20	- -	Compact	Compact	Compact

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[1] *Berg. und Hutt. Ztg.*, 1893, p 393.

According to Nahnsen other salts of zinc showed similar relations between temperature and current density, but the limits of current strength and temperature are different from those obtaining in the case of sulphates. For instance, a solution of zinc nitrate, moderately concentrated, evolved hydrogen even at 0° C. with a current density of 9·4 ampères per square foot; whilst such evolution no longer occurred at − 12° C. Whilst Kiliani, using a solution of zinc sulphate of 1·38 specific gravity, with a current tension of 30 ampères per square foot, obtained a deposit of zinc which could be readily wiped off, Nahnsen at a temperature of + 30 C. obtained from a solution of zinc sulphate of approximately equal concentration with a current density of 18·8 ampères per square foot a perfectly solid deposit of zinc. When large electrodes, 3 feet 3 inches by 1 foot 8 inches, were used, the latter obtained at a temperature of + 21 C. an unexceptionable deposit of zinc with a current density of 7 ampères per square foot. When he employed electrodes of 5·4 to 10·8 square feet in area, he obtained good zinc with a far less current density than could have been expected from the experiments carried out with the above electrodes of 0·05 square foot in area. The high current tensions found by Kiliani are explained by him by the circumstance that the latter worked with small electrodes; and he ascribes the fact that the influence of current density and of temperature upon the nature of the zinc deposit decreases with the increase of the area of the electrodes, to the action of the edges of the latter. The current density is greater at the edges of the electrodes than in the centre part, and therefore diminishes the average total density, this diminution being the more noticeable the smaller the electrodes are. Up to the present, however, experiments are wanting to determine the effect of temperature above the given limits upon the character of the zinc deposit, and thus to enable a correct opinion to be formed upon the subject. Coehn[1] is of the opinion that the formation of spongy zinc is due to the evolution of hydrogen, and states that the formation of this body can be prevented at the cathodes even with low current density by interrupting the current from time to time. Thus he claims to have produced a compact deposit with a current density as low as 4·7 ampères per square foot in the electrolysis of zinc sulphate by interrupting the current 50 times per minute. During the interruption the current was made to traverse a second bath, these interruptions being produced by special mechanical contrivances. Cowper-Coles[2] attempts to produce dense deposits of zinc by increasing the current density from time to time in intervals of about

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[1] D. R. Patent, No. 75,482, 1893.

[2] D. R. Patent, No. 79,447, 1894.

8 minutes. Hoepfner[1] considers that an active motion of the electrolyte by means of rotating cathodes is necessary for the production of dense deposits. Mylius and Fromm[2] agree with Nahnsen in ascribing the cause of the formation of spongy zinc to the formation of zinc oxide or of basic salts. If the conditions are not favourable to the formation of zinc oxide, no sponge is produced. On dissolving zinc sponge in mercury they always obtained a residue containing zinc oxide or a basic salt, the amount of which was less than 1 per cent. of the weight of the sponge. If oxidising agents were present during the electrolysis of a solution of zinc sulphate, zinc sponge was always formed, whilst in the absence of such bodies deposits of smooth white zinc were obtained. For example, a 10 per cent. neutral solution of zinc sulphate, with a current of 10 ampères per square foot, formed sponge at the end of two minutes in the presence of 0·01 per cent. of hydrogen peroxide. When the electrolyte contained 0·1 per cent. of zinc nitrate as an oxidising agent, a blackish-gray deposit of zinc containing oxide formed at the end of one minute. This deposit contained zinc nitrate and requires further investigation. A cathode of sheet zinc which had been touched in several places with turpentine containing oxygen, showed at once the commencement of the formation of zinc sponge by the development of grayish-black stains at the spots that had been touched. From a 10 per cent. solution of sulphate of zinc into which zinc oxide had been stirred, with a current density of 10 ampères per square foot, five minutes after the commencement of the electrolysis gray spongy zinc was deposited upon the cathode of sheet zinc in a streak along the surface of the solution. The presence of foreign metals in the electrolyte promotes the oxidation of zinc, and therefore the formation of sponge. Although Mylius and Fromm thus ascribe the sponginess of zinc to zinc oxide, they do not altogether exclude the possibility that hydrogen may play a part in its formation. According to their views, sponge cannot be deposited from acid solutions of sulphate of zinc. The experiments of Mylius and Fromm have reference to soluble zinc anodes.

Ashcroft found in a large number of experiments that the formation of spongy zinc was always connected with the evolution of hydrogen, and that zinc oxide was not deposited direct upon the cathodes, but was only produced by the decomposition of zinc sponge already formed by the action of water. According to Ashcroft's experiments, the formation of spongy zinc is completely prevented in solutions of zinc chloride, which also contain sodium sulphate, by the addition of certain oxidising agents, such as potassium permanganate, potassium chlorate, chlorine or chloride of lime. He also found that less zinc was always deposited from acid zinc solutions than is required by theory (18·7 grains per ampère per hour), whilst a larger quantity than the theoretical was always deposited from basic salts. In some cases he obtained from such solutions 50 per cent. more than the theoretical output. In experiments of this kind, which the author had the opportunity of witnessing in London, hot solutions of zinc chloride, saturated with zinc oxychloride, were used and produced firm, white and compact zinc. After 8 hours the solution had become neutral and had to be saturated again with zinc oxychloride to keep the deposit in the above condition During the first 2 hours of the operation the excess of zinc deposited above the theoretical quantity was 49 per cent.; in the next 2 hours 37 per cent.; in the next 2 hours 14 per cent.; and in the last 2 hours the theoretical quantity only. On continuing the electrolysis the quantity of deposited zinc fell below the theoretical quantity, the zinc became spongy, and after a comparatively short time no more zinc was thrown down.

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[1] English Patent, No. 13,336, 1893.

[2] *Zeitschr. f. Anorg. Chemie*, vol. xix., 1895.

According to Siemens and Halske, the formation of spongy zinc is due to the presence of small quantities of hydrogen and traces of zinc hydride (ZnH_2). To avoid this objection,[1] they propose to fix the hydrogen by means of free halogens, or by such halogen compounds as will combine with the hydrogen with the formation of the respective hydrides. Among such bodies applicable to a solution of sulphate of zinc may be named a weak solution of chlorine, bromine or iodine, or a weak solution of free hypochlorous or hypobromous acid, or chlorine or bromine gas, or chlorine and bromine substitution products of organic bodies which are soluble in water, and which give up their chlorine or bromine, and are thus reduced to lower compounds by nascent hydrogen, as, for instance, the soluble chlorhydrine of glycerol, and other glycols. When an excess of chlorine is present in the solution of zinc sulphate, hypochlorous acid always forms according to the following equation :—

$$2ZnSO_4+2H_2O+2Cl_2=ZnCl_2+Zn(HSO_4)_2+2HOCl.$$

The chemical changes that take place when the above bodies are added are the following :—Free chlorine forms hydrochloric acid with either hydrogen or with the hydrogen of zincic hydride, as is shown in the following equations:—

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[1] D. R. Patent, No. 66,592.

$$ZnH_2 + Cl_2 = Zn + 2HCl$$
$$H + Cl = HCl.$$

As these substances are only employed in very small quantities, the hydrochloric acid produced is too dilute to have any dissolving action upon the cathode. The dilute hydrochloric acid, however, forms free chlorine with hypochlorous acid formed as above, as shown in the following equation:—

$$HCl + HOCl = H_2O + Cl.$$

Hypochlorous acid or hypobromous acid acts as follows upon zincic hydride and hydrogen:—

$$ZnH_2 + HOCl = Zn + H_2O + HCl$$
$$H_2 + HOCl = H_2O + HCl.$$

The zinc chloride formed by the action of chlorine upon zinc is transformed into zinc sulphate by the sulphuric acid liberated at the anode and diffusing from it through the solution, as shown by the following equation:—

$$ZnCl_2 + H_2SO_4 = ZnSO_4 + 2HCl.$$

The hydrochloric acid thus formed again forms free chlorine with the hypochlorous acid.

The chlorine liberated in these various reactions continually acts over again in the above manner. In the presence of hypochlorous acid in the solution the chlorine is accordingly regenerated to a very large extent. Zinc deposited with the addition of these bodies is said to be compact and of a silvery colour. It is necessary, in conducting the process, that the fluid to be electrolysed shall constantly show a distinct reaction of the free halogen or of the active oxycompound of that halogen.

Mylius and Fromm[1] consider that the above opinion of Siemens and Halske, that the formation of zinc sponge can be prevented by the destruction of zinc hydride as above, is not tenable. They refer the action of chlorine, iodine, hypochlorous acid, &c., merely to the fact that these bodies are acid-formers. According to Borchers[2] it has not been proved that zinc hydride is formed when zinc salts are electrolysed. He is of the same opinion as Mylius and Fromm, and adds that in the presence of sulphurous acid, phosphorous and hypophosphorous acids, *i.e.*, of reducing agents, he has obtained the same results as were produced by Siemens and Halske by means of chlorine, bromine, iodine, &c. According to the experiments of Nahnsen, zinc is thrown down in the spongy form when the solutions of zinc salts are rendered impure to any great extent by the presence of other metals. In addition to the absolute quantity of these foreign bodies present, the strength of the zinc solution and the density of the electric current are also important. With 1 lb of zinc to 1 gallon of solution, 0·004 oz. of copper in the gallon have, according to Nahnsen, no effect upon the character of the deposit. With ½ lb. in 1 gallon there is a distinctly perceptible evolution of gas. With 0·016 oz. to the gallon there is evolution of gas and the deposit at the same time becomes slightly warty. With 0·024 oz. this wartiness appears earlier and more strongly marked; and with 0·048 oz. in the gallon the zinc is thrown down in the spongy form.

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[1] *Zeitschr, f. Anorg. Chem.*, vol. ix., 1895, p, 144.

[2] *Electro-Metallurgy*, 1896, p. 283.

With 3·2 oz. of zinc in the gallon of solution as little as 0·0016 oz. of copper in the gallon already produces a few scattered spots. With 0·008 oz., the whole electrode becomes warty, and with 0·02 oz. of copper in the gallon the deposit already becomes spongy at the end of 55 minutes. Cadmium, silver, arsenic and antimony are said to behave like copper; iron is said to promote the evolution of hydrogen and to render the baths impure by the separation of ferric and ferrous oxides, without having, however, any influence upon the formation of spongy zinc, as long as the quantity is not excessive. For instance, according to Nahnsen, with 3·2 oz. of zinc and 0·32 oz. of iron as protoxide in the gallon of solution, no sponginess was noticeable; neither was there with the same amount of zinc and 0·4 oz. of iron in the form of peroxide.

Mylius and Fromm[1] assume that those foreign metals which promote the oxidation of zinc electrically, give rise to the formation of sponge. According to their experiments, on the electrolysing of a 10 per cent. solution of zinc sulphate, which contained 0·004 per cent. of arsenic as ammonic arsenite, at the end of a minute zinc sponge was produced. Nahnsen proposes first to precipitate, by means of lime or a similar re-agent, both the zinc and the foreign metals from the crude solutions, and to treat the precipitate thus obtained with the acid electrolyte escaping from the baths. The latter, after it has been neutralised, traverses a series of vessels in which it comes in contact with zinc dust, which precipitates the metals which are electronegative towards zinc, an equivalent quantity of zinc passing into solution. Iron generally occurs in the neutral or feebly basic solutions as proto-salt. It can only be precipitated out of the solution after conversion into a per-salt. According to a patent of the company which has acquired Egestorff's Salt Works,[1] iron can be removed from solutions of sulphate by the addition of carbonate of lime, and passing a current of air through the solution. If the iron is present as chloride and not in too large quantity, it is best oxidised and precipitated by the addition of a small quantity of chloride of lime, the calcium chloride so formed having no injurious effect upon the electrolysis. If the quantity of iron present is exceedingly small, the iron is best oxidised by a solution of a chromate and precipitated by the simultaneous addition of soda, zinc oxide or zinc carbonate. Both the iron and chromium are thus thrown down in the form of hydrates, as shown in the following equation, sodic chromate and soda being employed:—

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[1] *Loc. cit.*

$$6FeCl_2 + 2Na_2CrO_4 + 4Na_2CO_3 + 12H_2O = 3Fe_2H_6O_6 + Cr_2H_6O_6 + 12NaCl + 4CO_2.$$

According to Pfleger[2] basic zinc salts ($ZnCl_2$, $3ZnO$, or $ZnSO_4$, $4ZnO$) are to be added to the solutions of zinc to purify the latter and to produce a basic electrolyte, previous to electrolysis. At the same time foreign metals are thus to be precipitated as basic salts, hydrates or oxides, by which means the solution of foreign metals, which may be present in the zinc anodes, as also the formation of spongy zinc at the cathodes, are said to be prevented. If the anode contains insufficient zinc, and the basic character of the electrolyte is in consequence diminished, care must be taken to replace the zinc oxide from time to time. As pointed out by Borchers, when zinc solutions contain proto-salts of iron, these must be oxidised to per-salts by means of chloride of lime, sodic hypochlorite, or by chromates before the basic zinc salts are added.[3]

Pertsch[4] assumes that the formation of spongy zinc in the electrolysis of solutions of zinc chloride is due to the formation of haloid acids, oxychlorides, basic oxychlorides, and other imperfectly known compounds. To prevent the formation of sponge, he adds a solution of zinc oxalate in aqueous oxalic acid to the electrolyte. In the presence of this salt the formation of chlorous and hypochlorous acids is said to be prevented, nor is any notable amount of water decomposed. The action of the zinc oxalate depends upon the easy decomposability of this salt into metal and acid radical. Oxalic acid used in this process is destroyed in consequence of its decomposition by polarising bodies. If, therefore, the process were even to work satisfactorily it would be too expensive.

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[1] D. R. Patent, No 23,712.

[2] U. S. A. Patent, 495,937, April 19, 1893.

[3] *Jahrb. d. Electro Chem.*, 1895, p. 164

[4] D. R Patent, No 66,185.

Lindemann[1] has found that a compact and perfectly pure deposit of zinc can be obtained from a solution of zinc sulphate, if zinc sulphide is maintained in suspension in the solution. the sulphide being precipitated by sulphuretted hydrogen from a neutral solution of zinc sulphate. This process has not yet come into use. It would seem, therefore, that a wide field still remains open to investigation to solve the exact reason of the formation of spongy zinc.

We have now to distinguish —

1. The extraction of zinc from ores
2. The extraction of zinc from alloys.

1. *The Extraction of Zinc from Ores*

When zinc is to be extracted from ores, the solution should, as a rule, be produced apart from the electric circuit. In the majority of the processes proposed up to the present, the zinc is dissolved in the form of sulphate or of a double sulphate, as chloride or a double chloride in combination with alkalies or alkaline salts, or combined with vegetable acids, the metal being deposited from these solutions by means of the electric current. Unless other metals are to be dissolved from the anodes, it is necessary to work with insoluble anodes. An evolution of gas is thus produced, and a great consumption of electric energy is rendered necessary. At the same time this evolution of gas tends to the formation of spongy zinc. Much attention has been given to overcoming these objections as far as possible by means of acid depolarising agents, and by employing electrolytes which are good conductors, and in some instances good results have been obtained. The various depolarising agents will be described under the individual processes to be mentioned below.

A general method of depolarising, proposed by Borchers, which has not yet, however, been employed practically, will alone be referred to here. Borchers proposes in consequence of certain experiments carried out by him, to employ oxygen separated in the course of electrolysis as an oxidising agent for certain organic compounds in place of the oxidising agents, such as peroxides, permanganates, chromic acid, arsenic acid, &c., hitherto used, and thus to combine the electrolysis of the metal with a process of oxidation to the advantage of both operations. The material for his oxidation process he finds in various distillation products of coal tar, such, for example, as the cresols. By mixing and digesting these substances with concentrated sulphuric acid they are readily converted into cresol-sulphionic acids, which are good conductors and are readily soluble in water. In the course of a sufficiently long-continued electrolysis, these are oxidised to carbon dioxide, water and sulphuric acid. If, however, the electrolysis is interrupted at a suitable time, according to Borchers, the whole series of the theoretically possible intermediate oxidation products can be obtained. It is a necessary condition for the combination of electrolysis with the processes of oxidation, that the oxidation product formed shall be readily separable from the solution that has to be electrolysed. In experiments carried out with such materials, Borchers with a current of 4·6 to 5·6 ampères per square foot obtained a brilliant and compact deposit of zinc. In order to maintain this current density, a tension, according to the proportion of zinc in the electrolyte, of from 1·5 to 2 volts was required. When currents of 14 ampères per square foot and an initial tension of 3 volts were employed, Borchers obtained good zinc, but the bath rapidly heated and increased the tension to such an extent that the work became unprofitable. The quantity of zinc which can be calculated upon in this method of depolarisation is given by Borchers as at the utmost 0·9 lb. per hour per horse-power. Nothing is yet known about the practical execution of this project.

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[1] D. R. Patent, Kl. 40, No. 81,640.

[2] *Op. cit.*, p. 98.

With the employment of insoluble anodes the tension in the bath averages 3 to 4 volts. When calculated for zinc sulphate from the calorific effect Q and from the quantity of current required according to Faraday's law for the decomposition of an electro-chemical molecule :—

$$(\gamma):p = \frac{Q \cdot 41691\,V \cdot Cb}{v \cdot \gamma \cdot Cb} = \frac{Q}{v}\,0{\cdot}433 \text{ volt},$$

the tension amounts to 2·29 volts, v being the number of electro-chemical molecules in one molecule. According to Killiani the tension, when carbon anodes are used, must be at least 2·5 volts to prevent the deposition of zinc oxide, together with the zinc. The power which is required to precipitate one kilogramme of zinc per hour from solutions of zinc salts, and with a tension of 2·5 volts in the bath, can be calculated as follows :—

To deposit one kilogramme (2·2 lbs.) of zinc per hour, 820·3 ampères are required. At a tension of 2·5 volts the power required amounts to $\frac{820{\cdot}328 \times 2{\cdot}5}{75 \times 981} = \frac{2058}{735} = 2{\cdot}80$ h.-p. As, however, a horse-power does not produce 735 watts, but 12 per cent. less = 650 watts in consequence of the power lost when mechanical work is converted into electricity, and as the older dynamos wasted 25 per cent. of the current in consequence of the conversion of the latter into heat, &c., the horse-power must be reckoned as $\frac{2{\cdot}80}{0{\cdot}38 \times 0{\cdot}75} = 4{\cdot}24$ h.-p. For a tension of 3 volts in the bath the horse-power may similarly be calculated as amounting to 5·06 h.-p. If 2 kilogrammes of coals are reckoned per horse-power per hour the quantity of coal consumed for 1 kilo of zinc would amount to 8·48 and 10 kilos respectively. With modern steam engines working with high pressure, expansively, and condensing, the loss of power in the conversion of mechanical work into electricity may be estimated at 9 per cent., whilst in the modern dynamos 6 per cent. of the original power is lost, so that a total loss of power of 15 per cent. occurs. To this may be added 10 per cent. of the current lost in the conductors, whilst the consumption of coal per horse-power per hour amounts in modern steam engines to 1 to 1·5 kilos of coal. Having regard to these considerations therefore, the consumption of power and of coals may be calculated at a lower figure than that given above.

As regards the extraction of zinc from the ores by means of electrolysis, it is but rarely perfect, as when zinc is leached out by means of dilute acids certain quantities of metal generally remain in the residues. This is especially the case when the ores contain iron, as is generally the case. If ferriferous zinc blende is calcined, as required for the production of zinc salts, a certain portion of the zinc oxide formed becomes insoluble in dilute acids and very difficultly soluble in hot concentrated acids. According to communications from Nahnsen the extraction of zinc from Upper Silesian ores, which contain 5 to 25 per cent. of iron, varies between 97 and 80 per cent. From Rhenish and Belgian ores containing very little iron, zinc is said to be extracted down to 2 per cent., and even less. The presence of lead has no effect upon the extraction of zinc as long as particles of zinc blende are not enveloped in the sulphate of lead formed from the sulphide during calcination.

(*a*) *The Extraction of Zinc from Zinc Ores Proper*

The extraction of zinc from zinc ores proper has up to the present nowhere come into use, and having regard to the power required, as stated above, for the deposition of the zinc, as also for the difficulties connected with the production of compact zinc, there seems but little likelihood of its introduction upon a working scale in the immediate future. The extraction of zinc from solutions of sulphate and chloride, combined with dissolving the zinc out of its ores within the electric circuit, had been proposed in 1880 by Luckow,[1] but has never come into use upon a large scale. The patent covers the production of zinc by the electrolysis of concentrated solutions, the acids or the chlorine thus liberated being allowed to act upon the zinc ores, whilst polarising is prevented by mechanical or chemical means. The decomposing cells are to be formed of wooden vats; sheets of zinc are to be used as cathodes, and wire baskets as anodes, these containing mixtures of carbon and zinc ores or zinciferous metallurgical products, or baskets or boxes made of wire and filled with carbon only. The zinc, which is said to separate out at the cathode in the form of grains, is to be caught on frames covered with cloth, arranged beneath the cathodes. By employing a solution of chloride of zinc or a feebly acid solution of common salt as the electrolyte, and a mixture of coke and zinc blende as the anode, the chlorine evolved during the electrolysis was said to decompose the blende and dissolve the zinc. When the anode consists of carbon alone, the chlorine produced was either to be removed mechanically by forcing in air, or chemically by forcing in sulphur dioxide. This process has not been employed on a working scale. The employment of ores as anodes, or the dissolving of zinc out of them in the bath, is not capable of execution. Chlorine attacks calcined zinc ores not at all, and blende but slightly. The zinc is, moreover, deposited in the spongy form.

The process of Letrange,[2] which was tested at St. Denis, in France, upon a large scale, depends upon the transformation of zinc blende into the sulphate outside the electric circuit, and the deposition of the zinc from the sulphate by means of the electric current. In this process depolarisation was not attempted. The ores at St. Denis were blendes, which were exposed to a sulphatising calcination in reverberatory furnaces, or were burnt in kilns, and then brought into contact with the sulphur dioxide produced during calcination. By means of the calcination a portion of the sulphide of zinc was converted into sulphate, another into zinc oxide. By means of sulphur dioxide the zinc oxide was converted into zinc sulphite, which in the course of time was oxidised to zinc sulphate by exposure to the air. The blende thus prepared was transferred to leaching vats, in which it was treated with water or with the acid solutions obtained in electrolysis. The zinc sulphate solution thus obtained was run first into a collecting tank, and thence into the baths. These latter were vats with double bottoms; the zinc solution was introduced into the interspaces between the two bottoms, and rose up through perforations in the upper one. The anodes consisted of plates of carbon, the cathodes of plates of brass or zinc. As it slowly ascended, the zinc solution gave off a considerable portion of its zinc contents to the cathode, and thus reached the upper portion of the tank, whence it flowed through an overflow tube into a collecting tank. From this tank it was made to pass over roasted ore in order to saturate itself with zinc and to be again electrolysed. The arrangement of the plant is shown in Fig. 158. *A* are the vessels for leaching the calcined blende; *B* is the collecting tank for the solution; *C* are the baths; *c* are the plates of zinc or brass placed opposite to the plates of carbon forming the anodes; *o* are the openings for the overflow pipes; *d* are the tubes which convey the solution to be electrolysed under the false bottom of the baths. The acid electrolysing solution is lifted by means of the pump *P* out of the collecting tank placed beneath it into the vessel *R*, from which it passes into the leaching tanks *A*. The zinc is said to have been deposited at the cathode in the form of sheets, and when its thickness reached 0·16 to 0·2 inch, it was stripped off from the cathode by means of a knife. The zinc contained iron, because ferric sulphate was dissolved out from the calcined blende. The current density and tension employed in this process are not stated; as no depolarising took place, these must have been so high as to

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[1] D. R. Patent, No. 14,256.

[2] *Berg. und Hütt. Ztg.*, 1882, p. 489; *Dingl.*, vol. 245, p. 455; *Austrian Pat.*, November 12, 1881.

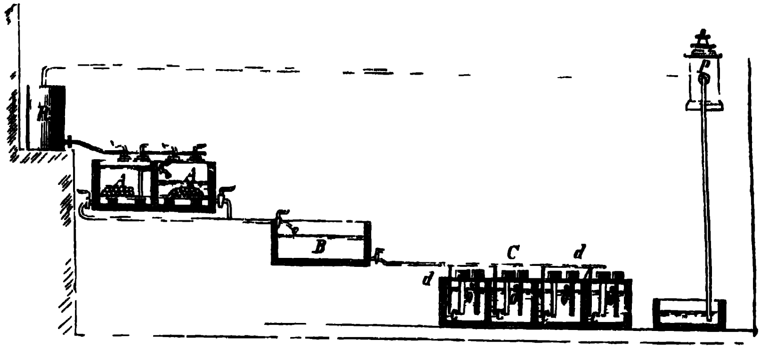

Fig. 158.

compel the abandonment of the process. The zinc may also have been deposited in the spongy form. In the literature on the subject,[1] the amount of zinc deposited per hour per horse-power is given as 1·3 lbs., which is far too high a figure. It probably did not amount to 0·4 lb. The consumption of coals per hour per horse-power may be assumed on the average as about 4½ lbs. It is therefore readily explicable that when the power required for electrolysis has to be obtained by the combustion of coal, the extraction of zinc in the dry way comes cheaper than the electrolytic extraction of zinc from solutions of sulphate in the above fashion.

Hermann[2] has attempted to improve the process by the employment of double salts of zinc sulphate and sulphates of the alkalies, of magnesium or of aluminium. Nahnsen has also recommended the addition of alkaline sulphates to solutions of zinc sulphate; it is at any rate a fact that zinc sulphate containing double salts was employed by Nahnsen in his experiments for working the zinc ores at Lipine in Upper Silesia. Nahnsen's process, which is kept secret, has been tried experimentally at the works of the Silesian Company for zinc mining and smelting in Lipine, and is said to have been proved technically feasible. The composition of the electrolyte is kept secret. It can only be said that it consists of zinc sulphate in combination with other salts which are not decomposed at the tension of the current employed. According to the process patented by Nahnsen,[3] the electrolyte contains 7 to 14 oz. of crystallised zinc sulphate and 1·5 to 3 lbs. of alkaline sulphate in the gallon according to the strength of the current. Nahnsen has communicated the following to the author respecting his process:—

"The ores (blende) are first calcined in the same way as for distillation; they are then brought into contact with hot acid solutions as these leave the baths, the zinc being thus extracted from them. The zinc solution is neutralised and clarified, treated in tanks with zinc dust for the precipitation of any electro-negative constituents that may be present, and then returned to the baths. The essential apparatus in this plant is that used for the solution of the zinc, which is so arranged upon the principle of opposing currents, that the zinc ores are fed in automatically and the residues free from zinc automatically removed. The whole process consists of the following two phases:—(1) Decomposition of the electrolyte in the bath into zinc and sulphuric acid; (2) transfer of the sulphuric acid or of the acid solution into the dissolving apparatus, where it is saturated with zinc from the ores. It is essential for the execution of the process that solutions free from iron should .be obtained. This object is attained by allowing the acid solutions in the dissolving tanks to come in contact with ores containing continually increasing percentages of zinc so that any oxide of iron in the solutions is rapidly precipitated by the oxide of zinc. By this means solutions of zinc sulphate free from iron are obtained. Any electro-negative metals that may be present in the solutions are precipitated by means of zinc dust."

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[1] *Berg. und Hütt. Ztg.*, 1883, p. 287.

[2] D. R. Patent, No. 24,682, April 24, 1883.

[3] D. R. Patent, No. 71,155.

The zinc is obtained pure and in a compact form. With plates 0·8 inch thick, the loss on melting is about 4 per cent. The zinc contains 99·9 per cent. of metal. According to Nahnsen the question of apparatus is the important one in carrying out this process on a large scale, but the results obtained experimentally admit of the conclusion that in this respect too the proper methods are being followed. The process has not yet, however, come into use.

Lindemann[1] proposes to throw down by means of the electric current very pure zinc in the compact condition from solutions of zinc sulphate in which zinc sulphide is suspended. The sulphide of zinc is produced by precipitating a solution of pure zinc sulphate of 37° to 38° B. by means of sulphuretted hydrogen. The electrodes consist of rolled lead. They are 0·4 inch apart, and the current density employed in the experiments amounted to 10 ampères per square foot; the tension, which is not stated, may be taken as 3 to 4 volts. The cathodes were subsequently to be replaced by electrolytic deposits of zinc with their edges cut smooth. The anodes, which gradually become covered with a superficial layer of peroxide of lead, must be freed from the latter by being washed from time to time. As soon as the bath contains 9 to 9½ ounces of free sulphuric acid per gallon, a current density of 10 ampères per square foot can no longer deposit zinc from it. Before therefore the free acid present reaches this amount, the electrolyte must be replaced by a neutral solution of zinc sulphate. The zinc sulphide, which is gradually decomposed by the acid liberated, must be renewed from time to time. This process has not yet come into use.

Siemens and Halske[2] propose for the extraction of zinc from its sulphide a process similar to that for the extraction of copper from ores containing copper sulphide,[3] in which polarising is partly prevented by the secondary action of the anion upon the electrolyte The slightly roasted zinc blende is to be treated outside the electric circuit with a solution of ferric sulphate containing free sulphuric acid, whereby the zinc is dissolved in the form of sulphate, ferrous sulphate being at the same time produced, and sulphur separated out, two molecules of ferrous sulphate being formed for every molecule of zinc sulphate, as shown in the equation :—

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[1] D. R. Patent, Kl. 40, No. 81,640.

[2] D. R. Patent, No. 42,243.

[3] Vol. i., p. 240.

$$ZnS + Fe_2(SO_4)_3 = ZnSO_4 + 2FeSO_4 + S.$$

The solution of zinc thus obtained is conducted into the bath, first to the cathodes, and then to the anodes At the cathodes a portion of the zinc is deposited, whilst the acid radical, SO_4, goes to the anode. The solution from which a portion of its zinc has been removed flows to the anode where the ferrous sulphate is re-converted by the anion, SO_4, into neutral ferric sulphate $Fe_2(SO_4)_3$. This ferric sulphate is then caused to act upon a fresh quantity of sulphide of zinc. By the oxidation of ferrous to ferric sulphate at the anode, an amount of electric energy equivalent to the heat of combination thus produced is evolved, and this partly counteracts the back electro-motive force produced by the decomposition of the zinc sulphate at the cathode. The process of electrolysis is expressed by the equation :—

$$ZnSO_4 + 2\,Fe\,SO_4 = Zn + Fe_2(SO_4)_3.$$

This process has never come into use in any way, nor is it likely to be introduced. The solution of zinc sulphide is very slow and very imperfect, and the electrolyte contains very large quantities of iron.

Coehn [1] proposes to use accumulator slabs of lead oxide as anodes for the electrolysis of oxy-salts of zinc, such as the sulphate. During the electrolysis, the lead oxide is converted into lead peroxide, and the plates are then to be used for the generation of electricity in lead peroxide and carbon elements with sulphuric acid. Nothing is known as to the practical execution of this process.

The process of Gunnar Elias Cassel and Frederik A. Kjellin, of Stockholm,[2] avoids polarisation by the employment of anodes of metallic iron or of some other metal, a plate of zinc forming the cathode. The anodes and cathodes are separated by a diaphragm of porous clay or some other suitable material. The cathode compartment contains the solution of sulphate of zinc to be electrolysed, which has been produced by the leaching of calcined blende with sulphuric acid. The anode compartment contains sulphate of iron or a sulphate of the metal employed as anode. Zinc is thrown down at the cathode by means of the current, whilst the acid evolved at the anode dissolves an equivalent quantity of iron. The object of the diaphragm is to prevent the intermixture of the solutions contained in the cathode and anode departments. The ferrous sulphate formed at the anode is to be sent into market as green vitriol. Although compact zinc may be obtained by this process with the employment of a comparatively small quantity of electrolytic energy it must, nevertheless, be borne in mind that fresh acid has to be constantly used for the production of the zinc solution, and that green vitriol is low in price and has a very restricted market. On the other hand, by leaching the calcined blende by means of water, as proposed by the patentees, a portion only of the zinc contents of the blende is brought into solution. Finally, it is highly possible that the deposited zinc will contain iron.

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[1] D. R. Patent, No. 79,237, 1893.

[2] D. R. Patent, No, 67,303.

The conversion of zinc into chloride from its ores and the electrolysis of the solution obtained has been tried experimentally at Bleyberg, in Belgium.[1] The solution of zinc was produced by treating calamine or calcined blende with hydrochloric acid. Any iron that passed into solution was precipitated by means of chloride of lime. The anodes consisted of graphite or carbon; the cathodes were sheets of zinc. The chlorine evolved at the anode does not seem to have been employed for the manufacture of bye-products; even though it had thus been utilised, the process would be too dear for zinc ores proper, as the chloride of zinc would have to be produced by treating the ores with hydrochloric acid, or with ferric chloride, or by means of a chloridising roasting. At Bleyberg a kilo of zinc is said to have required 9 h.-p. hours, or 18 kilos of coal. The process has not come into use for zinc ores.

Hintzerling[2] proposes to dissolve oxide of zinc out of calcined blende or calamine or metallurgical products containing zinc oxide, by means of magnesic chloride, and to electrolyse the solution obtained. The zinc is said to be deposited by means of a current tension of 19 ampères per square foot from the solution of chloride of magnesium containing zinc oxide; the solution of magnesium chloride, left after the zinc had been thrown down, was to be used for the solution of fresh quantities of zinc oxide. The baths containing zinc were to have been treated with from seven to fourteen times their quantity of magnesium chloride solution, of from 1·26 to 1·29 specific gravity, at the boiling point, best under a pressure of 2 to 3 atmospheres, the mass being kept in motion by means of stirrers. This boiling is best carried out in closed vessels, so as to prevent the formation of magnesic oxy-chloride. Any of this substance formed in the solution was to be converted into magnesic chloride by the addition of hydrochloric acid. Nothing is known as to the application of this process.

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[1] *Berg. und Hütt. Ztg.*, 1883, p. 367.

[2] *Dingl. Journ.*, Vol. 288, p. 263.

For extracting zinc from pyrites residues and from zinciferous silver ores the processes to be described below for converting the zinc into chloride and the electrolysis of the solution of chloride, have come into use. Blas and Miest[1] have proposed to crush ores containing sulphide of zinc, and to mould them into plates under a high pressure of about 100 atmospheres with the employment of a temperature up to 600°C., and to use these plates as anodes in the electric current. For the electrolyte a solution of zinc sulphate, chloride or nitrate was to be used. This process, which was based upon the conductivity of metallic sulphides for electricity, has not been found satisfactory; the plates, composed of non-homogeneous constituents, must fall to pieces tolerably rapidly in the course of the electrolysis, whilst all action must cease as soon as contact with the conductor is interrupted by the sulphur separated out from the particles of ore nearest to the conductor.

Extraction of Zinc from Solutions of Zinc Sulphite

Kosmann and Lange[2] propose to treat zinc ores (calamine or calcined zinc blende) with sulphur dioxide and water, and to throw down zinc from the solution of zinc sulphite thus obtained, by means of the electric current. The oxygen thereby evolved is said to be absorbed by the sulphur dioxide liberated by the decomposition of the salt, converting it into sulphuric acid. This process is said to require a lower current tension than the decomposition of zinc sulphate. Experiments on a large scale are said to have given 0·4 pound of zinc thrown down per horse power per hour. Kosmann states that by the employment of Wolff's locomotive type of engine with condenser, the consumption of coal per hour per horse power amounts only to 2·2 lbs., so that these 2·2 lbs. of coals are capable of producing 0·4 lb. of zinc. The process has not, however, come into use. Zinc sulphite is soluble in water only as an acid salt, and, when exposed to the air, is converted with tolerable rapidity into sulphate.

The Extraction of Zinc from Solutions in Organic Acids

This method has not come into use for ores; under this head should be included an English patent of Watt, No. 6,294, 1887, as also the proposal to use acetic or lactic acid as electrolytes.

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[1] *Essai d'Application de l'Électrolyse*, Louvain and Paris, 1882.

[2] D. R. Patent, No. 57,761.

The Extraction of Zinc from Alkaline Solutions

The deposition of zinc from alkaline solutions has not come into employment at all, and appears to offer no prospects. Kiliani[1] proposes to dissolve zinc from ores and metallurgical products by means of a solution of ammonia or fixed alkali, to which ammonic carbonate has been added, in separate vessels outside the electric circuit, and to electrolyse the solutions, cathodes of sheet zinc or sheet brass and anodes of sheet iron being employed. The zinc is said to be deposited at the cathode in the compact form, whilst a quantity of oxygen, equivalent to the metal deposited, is said to be liberated at the anodes. The solution escaping from the baths is collected in tanks and then pumped back into the dissolving baths, where it dissolves out a fresh quantity of zinc. There are no data with reference to the current density and tension. It is, however, undoubted that with equal current densities the electrolysis of such solutions would require a much higher tension than that of sulphite, sulphate or chloride; the alkalies are, moreover, dearer than acids. It may therefore be assumed that this process will not come into use.

Höpfner[2] leaches the zinc out of bodies containing zinc oxide (poor zinc and lead ores) by means of an alkaline solution, and conducts this solution to the cathodes of a bath for the deposition of the zinc, chlorine or chlorates of the alkalies or alkaline earths being produced at the cathodes by the decomposition of alkaline chlorides. The ores are ground fine and then brought into intimate contact with alkaline solutions in a dissolving tank provided with a stirrer. Any lead oxide that may be present is dissolved together with the oxide of zinc. After the solution has been freed from foreign metals by means of zinc dust, it is passed in a continuous stream into the cathode division of the electrolytic bath, which is separated from the anode division by a suitable membrane, or pair of membranes with a solution of soda or potash between the two. The zinc produced at the cathode separates out in the compact state, and does so the better the more thoroughly the solution is kept in motion. The anode division must contain a solution of chlorides to be constantly kept at a uniform degree of concentration, and also containing alkaline chlorides, as, for example, solutions of carnallite or of the final liquors of the ammonio-soda process. By means of the electric current chlorine is evolved at the anode whilst the alkalies pass into the cathode division, and unite with the alkali already present there. In consequence of the diffusion of alkalies or alkaline carbonates from the cathode space, oxychlorides are formed at the anode. The chlorine can be collected and used as such, or for the manufacture of bye-products. The evolution of free chlorine at the anodes can be prevented by adding alkaline earths to the solution in the anode compartment, and thus forming chlorates. The solution of chlorates can be worked up for the manufacture of potassic chlorate. Nothing is known as to the applicability of Hopfner's process to zinc ores proper. In a modified form it has been used for the extraction of zinc from pyrites residues.

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[1] D. R. Patent, No. 29,900, March 11, 1884; and No. 32,864, August 19, 1884.

[2] D. R. Patent, No. 62,964.

W. S. Squire and S. C. Currie[1] have attempted to extract zinc from an alkaline solution of the oxide with the employment of mercury as a cathode. The deposited zinc forms an amalgam with the mercury and is submitted to distillation, whereby zinc is obtained, and the mercury recovered.

Burghardt[2] attempts to extract zinc from a solution of sodic zincate, which is to be produced by fusing zinc ores freed from sulphur, such as dead roasted zinc blende, with soda and 3 to 4 per cent. of carbon, and leaching out the molten mass. The ore is to be packed around the anode by means of an asbestos cloth. Its zinc contents are to be oxidised there and thus brought into solution. Neither of these processes have found any application.

(b) *The Extraction of Zinc from Ores in which it is a Subsidiary Constituent*

Among the ores which contain zinc as a subsidiary constituent, only zinciferous pyrites residues have up to the present been submitted to electrolytic extraction of the zinc. It is probable that in the immediate future the extraction of zinc from argentiferous zinc ores or zinc-lead ores will be attempted.

Pyrites residues are the residues obtained in calcining pyrites containing zinc blende, the sulphur of which has been converted into sulphur dioxide and used for the production of sulphuric acid. They consist of ferric oxide, and variable quantities of zinc sulphide, oxide and sulphate. They can only be used as iron ores when the zinc has been removed from them; as long as they contain zinc they are worthless. In order, therefore, to make these residues valuable as iron ores on the one hand, and for the extraction of their zinc contents on the other hand, electrolytic processes have been proposed, and have recently come into use for the residues of pyrites from Meggen, which contain from 5 to 15 per cent. of zinc. Leaching these residues by sulphuric acid was found not to be profitable, as it was not possible to remove the whole of the zinc, and as the zinc vitriol produced found no market. The zinc was therefore converted into chloride either by a chloridising roasting of the residues (see page 198) or by treating them with solutions containing certain chlorides. The chloride of zinc was then dissolved and zinc extracted from the solution. Several works have been built and have started operations, viz., near Duisburg, at Führfurt on the Lahn, at Weidenau in Siegen, and at Homberg on the Rhine. The Duisburg Works are said to use a method devised by Kittler, and the Fuhrfurt, Weidenau and Homberg works a process of Hopfner, both of which are kept secret. At Duisburg, Hermann's electrolyte, namely zinc sulphate together with alkaline sulphates, is said to be employed. At the other works chloride of zinc is said to be produced by a chloridising roasting of the zinciferous residues, and the solutions containing chloride of zinc to be purified and then electrolysed. The chlorine at the anode is removed by means of an air current, and passes into chambers in which it is used for the production of chloride of lime. The author knows nothing about the details of the construction or of the commercial results obtained. A difficulty in the employment as iron ores of the pyrites residues freed from zinc, is occasioned by their fine state of division.

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[1] English Patent, No. 12,249, September 27, 1886.

[2] D. R. Patent, No. 49,682.

The extraction of zinc from argentiferous lead ores containing considerable quantities of zinc, such as occur for instance at Broken Hill in New South Wales, has not yet been perfected, but is, however, now being worked at. With cheap motive power, extraction of zinc from such ores electrically may probably be employed with advantage, seeing that the removal of zinc from these ores by means of dressing is not possible without great losses of lead and silver. For a portion of the Broken Hill ores, consisting of intimate mixtures of argentiferous galena and argentiferous zinc blende, a plant for the Ashcroft process is at present being erected at Newcastle in New South Wales. The author had an opportunity of examining the experimental plant for this process at Grays, in Essex, England. The process consists in converting the oxide of zinc in the calcined ores into chloride of zinc by means of ferric chloride, whereby the iron is separated as ferric hydrate and mixed with the ore. The ores thus freed from the greater portion of their zinc contents are smelted for argentiferous lead and the zinc is precipitated by the electric current from the solution of chloride of zinc, the solvent being at the same time regenerated. Sheet zinc is used for the cathodes, plates of cast-iron and afterwards plates of carbon being used as anodes. The chlorine evolved during the electrolysis combines with the cast-iron anodes to form ferrous chloride solution, whilst where carbon anodes are used it converts ferrous chloride into ferric chloride. Both by the formation of ferrous chlorides, as also by the conversion of the latter into ferric chloride, electric energy is introduced into the circuit. To prevent the deposition of iron at the cathodes the solutions of ferrous and ferric chloride are separated from the zinc chloride by diaphragms of cotton, the zinc chloride solution forming a higher column than the solution of the iron salts. From the solution of zinc chloride to be electrolysed first the iron is precipitated, and then the other metals which are electro-negative to zinc, and the solution is conducted first into the cathode department and then into the anode department of the bath, passing first to the iron and then to the carbon anodes. The baths provided with iron anodes form two-thirds, those with carbon anodes one-third of the total number. The solution escaping from the last carbon anode bath still contains a certain quantity of zinc, and is used for the solution of fresh quantities of zinc oxide from the calcined ores. The baths are arranged in circuit, the electrodes in the different baths being coupled in parallel. The current density amounts to 5 ampères per square foot, the tension in the baths with iron anodes to 1·1 volts, in those with carbon anodes to 2·7 volts. The quantity of zinc deposited per ampère hour is equal to at least the theoretical amount (18·67 grains); the consumption of power to precipitate one kilo of zinc amounts to 2½ horse-power hours, or if steam is used, to 3 kilos of coals. The zinc is obtained in compact form and is easily stripped off from the cathode sheets. It contains an excessively small amount of iron and therefore simply needs re-melting. Of the zinc contents of the ore, 66 per cent. are removed by the solution of ferric chloride, which contains 0·8 to 1 ounce of iron in the gallon. For 100 parts by weight of zinc 66⅔ parts by weight of iron are consumed, theory requiring only 57. The ferric chloride which is lost in the course of the process is replaced by the combination of the chlorine with iron during electrolysis of zinc chloride. Zinc chloride is obtained by decomposing zinc sulphate with common salt, the zinc sulphate being produced by a slow oxidising roasting of ores containing zinc blende. The advantages of the Ashcroft process are the following:—

1. The calcined ore is freed from the greater part of its zinc contents.

2. The ferric hydrate, formed on treating the calcined ore with

a solution of ferric chloride, forms a suitable flux for smelting the ores, serving to slag off the silica and the residual zinc, as also for the decomposition of the sulphide of lead, after the oxide of iron has been reduced to iron.

3. The solvent for zinc is regenerated in the course of the electrolysis.

4. By the formation of ferrous chloride and by the conversion of this salt into ferric chloride in the course of the electrolysis, a notable quantity of electrical energy is introduced into the circuit.

2. *The Electrolytic Extraction of Zinc from Alloys*

When zinc alloys are submitted to electrolysis, these form the anodes of the circuit, so that the back electromotive force is to a great extent counteracted. Both impure zinc, as also alloys of zinc with lead and silver, have been treated electrolytically. The electrolysis of zinc containing lead is carried out at the works of Aaron Hirsch at Ilsenberg in the Harz, water furnishing the motive power.

Zinc acetate is said to be used as the electrolyte. A pure zinc, free from lead, is obtained from impure zinc, and it fetches so high a price that the works are paying well. The process is kept secret. Rosing[1] has proposed a process for the electrolytic extraction of zinc from so-called zinc scum, an alloy of lead, silver and zinc, obtained in desilverisation. This method was tried experimentally for a while at the Frederick Works, in Upper Silesia, but has had to be given up because the distillation of zinc from the zinc scum was found to be cheaper than its electrolysis. The zinc is present in relatively small amount, and irregularly distributed in the scum. The latter is also so brittle that it cannot be moulded into plates. Rösing therefore employs the zinc scum in the form of powder, and arranges his electrodes horizontally. Round wooden vats were used as baths. The electrolyte was zinc sulphate; the anode consisted of a plate of lead lying on the bottom of the vat and covered with powdered zinc scum. Above the latter was the cathode, consisting of sheet zinc and supported upon insulators. Several vats were arranged, one above the other, so that the electrolyte could traverse them from above downwards. As soon as the zinc had been dissolved from the grains of the zinc scum to a certain depth, and the contact of the electrolyte with the zinc still contained in the zinc scum was thus gradually diminished, or almost prevented, the scum was removed from the baths and submitted to liquation to free the grains from the crust, which consisted of a mixture of lead and silver, and thus to obtain a fresh zinc surface for the action of the electrolyte. The liquated zinc scum was again submitted to electrolysis, and then again liquated. Liquation and electrolysis thus alternated until the greater portion of the zinc was removed from the scum. The residual argentiferous lead was cupelled. The zinc, which carried both lead and silver, was used for desilverising work-lead. As stated, this process has not come into use. At present, attempts are again being made at the Frederick works to electrolyse alloys of zinc, silver and lead, which are free from oxide.

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[1] D. R. Patent, No. 33,589; *Preuss. Ztschr.*, 1886, p. 91; *Dingl. Journ.*, 1887, p. 93.

At Hoboken, near Antwerp, until recently alloys of zinc and silver, which were obtained by desilverising work-lead by means of zinc containing aluminium,[1] were submitted to electrolysis. The anodes consisted of plates of the above alloy; the cathodes were sheets of zinc in the form of discs of 3 feet 3 inches in diameter, which were fastened to a horizontal spindle. This was situated above the surface of the bath, and was revolved so that half of the cathode was inside the solution, the other half outside it. By turning the cathodes the solution was kept in movement. The electrolyte consisted of a solution of chloride of zinc in chloride of magnesium of a specific gravity of 2·2 to 1·27. After the removal of the zinc from the anodes, these produce a mud consisting of 75 per cent. of silver and 12 per cent. of lead. Experience up to the present has not shown any advantage in electrolysis as compared to other methods of separating zinc from silver and lead. At Lautenthal, the aluminium process has been given up, and distillation is to be introduced. At Hoboken, also, the old process (desilverising with the addition of zinc and distilling off the zinc from the alloy) is now being used. The zinc so obtained is again used for desilverising work-lead. The apparatus of Bridgman[2] also depends upon the principle of keeping the solution in movement by means of rotating cathodes; its construction is shown in Figs. 159 to 162,[3] in which *A* is the tank containing the electrolyte. Within it rotates the shaft, *B*, protected by an insulator, *r*, and to which the cathodes, *E*, are secured by means of screws and wedges, these screws forming at the same time the connection between the cathodes and the conductors. *D* are the anodes, which are cut out as shown at *v*, so as not to interfere with the movement of the shaft. The detail of the construction of the cathodes is shown in Fig. 162. The sheet metal forming the cathodes, which is coated with graphite, is secured in the frame, *p'*, made of non-conducting material. It can be removed from these frames as soon as the deposit has attained the desired density; *q* is an opening provided with a locknut, *q'* through which the shaft passes.

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[1] Vol i., p. 562.

[2] U.S.A. Patent, No. 526,482, September 25, 1894.

[3] Borchers, *Electro-Chem.*, 1895, p. 164, Halle, A. S.

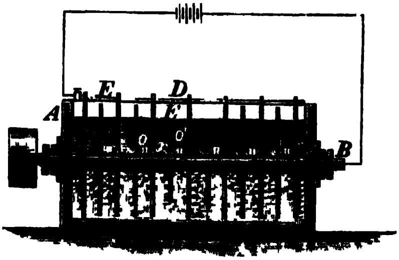


Fig. 159.

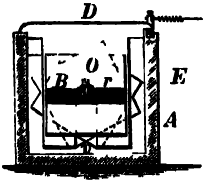


Fig. 160.

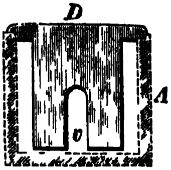


Fig. 161.

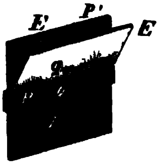


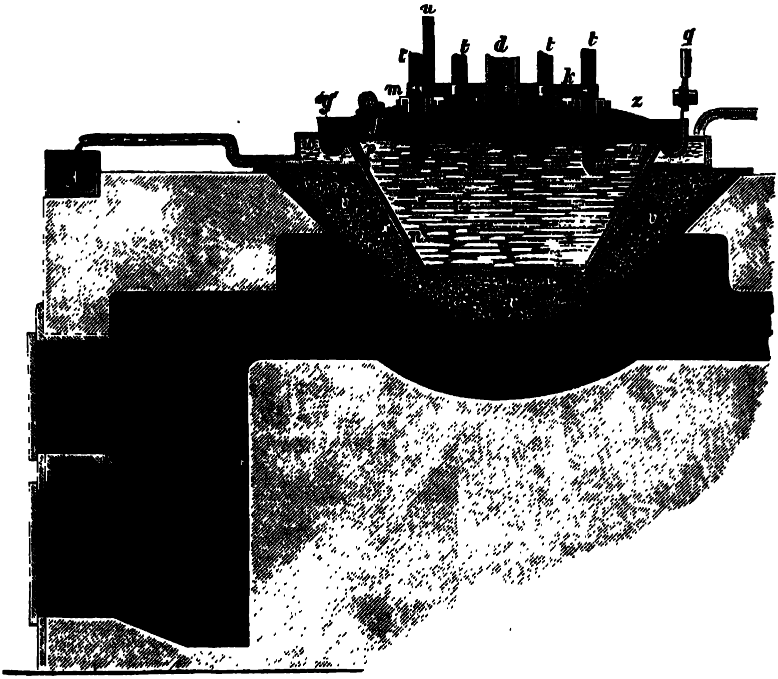
Fig. 162.

Projects for the Electrolytic Extraction of Zinc in the Dry Way

Up to the present, it has not been found possible to extract zinc electrolytically in the dry way. Proposals based upon laboratory experiments for the extraction of the metal on a large scale in this manner depend upon the electrolysis of molten zinc chloride, or of molten mixtures of zinc chloride with other chlorides, principally those of lead and silver. Borchers[1] proposed to electrolyse fused chloride of zinc between anodes of carbon and cathodes of sheet zinc with current densities of 100 to 200 ampères per square foot of cathode area, and tensions of 3 to 4 volts. He points out that the advantages of this process, which would produce zinc at the cathode and chlorine at the anode, the latter to be utilised in any desired manner, would be that with an equal consumption of power an apparatus for electrolysis would be five to ten times smaller than those required for the

[1] *Elektro Metallurgie*, 1896, p. 296.

electrolysis of aqueous solutions of zinc salts when insoluble anodes are employed, and that chlorine would be produced without the employment of diaphragms. With the above current densities, the tension, even when the current density at the anode is considerably greater than that of the cathode, is said not to exceed 3 to 4 volts. When aqueous solutions of zinc salts and insoluble anodes are employed, this tension is said to be exceeded even when the current density amounts only to 50 ampères per square foot. Borchers [1] has proposed an apparatus shown in Figs. 163 and 164 for the electrolysis of fused zinc chloride upon a large scale, Fig. 163 being a vertical section through the apparatus, whilst Fig. 164 shows a portion of the cover in plan; x is a lead vessel having the shape of an inverted truncated cone, which has at its upper part a groove, y, into which the cover, z, fits. A channel, w, in which water for cooling the apparatus



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[1] *Op. cit.*, p. 295.

circulates, surrounds the upper portion of the vessel. The leaden pan is set in an iron pan, *v*, filled with sand, which is heated by means of a grate. The electrolyte is contained in the leaden pan. The anodes are formed by rods of carbon, *t*, inserted through the cover of the pan and connected with each other by means of the annular clamp, *k*, this clamp being connected with the cable *u*. The individual carbon rods are surrounded by insulators, *m*, where they traverse the cover. The cathodes are formed by pieces of sheet zinc attached to the walls of the leaden pan and connected with the cable *q*. An opening in the middle of the cover, provided with a tubulure, *d*, serves to conduct away the chlorine evolved during electrolysis, a second opening, *f*, which can be closed when desired, serving for the introduction of the zinc chloride during the operation. The operation is to be conducted as follows :—Chloride of zinc is to be melted in the leaden pan until the molten mass fills the groove *y*. The cathode, *n*, is then introduced, the cover is put on, and cold water is allowed to flow through the channel *w*. The cover is kept suspended until a crust of salt, *p*, has formed in the groove and around the upper portion of the pan, when it is allowed to settle down; the current is then passed through, and on account of its great strength, such a quantity of heat is evolved that but little firing is required. The zinc deposits on as much of the cathode as is not protected by the crust of zinc chloride, the chlorine escaping through the tubulure *d*. Fresh chloride of zinc is added from time to time through the opening *f* in order to keep the pan constantly filled with the molten salt. When a sufficient quantity of zinc has been deposited at the cathode, the water current is cut off, so that the crust of salt in the groove, *y*, melts, when the cover can be removed, the cathode with the deposit of zinc taken out, and replaced by a fresh one. This apparatus of Borchers has not yet been employed practically. Lorenz[1] proposes to submit molten mixtures of the chlorides of zinc, lead and silver to electrolysis, when lead and silver are said to separate out first, and afterwards pure zinc to be deposited. This proposal too has found no practical application up to the present.

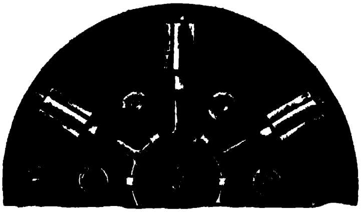

FIG. 164.

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[1] *Zeitsch. f. Electro-Chem.*, 1895-96, No. 15, p. 318.

Treatment of Ores containing Zinc for the Production of Merchantable Zinc Compounds

In many cases ores of zinc are treated in order to produce marketable compounds of zinc, such as zinc oxide, mixtures of zinc oxide, lead oxide and lead sulphate, and zinc vitriol. Such compounds of zinc are as a rule only then produced. when the zinc-bearing ores are not suitable for the extraction of metallic zinc, either because they contain other valuable metals, such as iron, lead or silver, or because they are too poor in zinc. Such ores are more particularly zinciferous iron ores and zinciferous lead or silver-lead ores. The extraction of zinc white is carried on in the eastern United States of North America, especially in New Jersey and Pennsylvania, the production of a mixture of zinc oxide, lead oxide and lead sulphate, in the States of Missouri and Colorado, and the production of zinc vitriol at the Julius and Sophia works in the Lower Harz.

Production of Zinc White

Zinc white is produced at the works of the Lehigh Zinc and Iron Company,[1] at Bethlehem, Pennsylvania, at the works of the New Jersey Zinc and Iron Company at Newark, New Jersey, at the works of the Passaic Zinc Company near Jersey City, and at the works of the Bergen Port Zinc Company at Bergen Port, New Jersey. The ore employed for the production of zinc white consists chiefly of a mixture of franklinite and willemite, with variable quantities of calamine and calcite. Zincite, rhodonite and tephroite also occur irregularly distributed in the mass. According to Dürre[1] the franklinite contains 9·20 per cent. of manganese, and willemite 2 to 7 per cent., the more rarely occurring rhodonite 42 per cent., and the also scarce tephroite 54 per cent. The average analyses of considerable quantities of these ore mixtures are as follows, according to Dürre :—[2]

	Taylor Mine.				Sterling Hill.	
	1	2	3	4	1	2
SiO_2 . . .	10·21	11·08	10·33	11·77	4·86	5·15
Fe_2O_3 . .	31·41	27·54	30·36	30·91	30·33	27·62
MnO . .	15·84	17·63	15·95	10·27	12·30	13·09
ZnO . . .	32 83	35·88	26·34	25·71	29·42	23·38
Al_2O_3 . .	0·21	0·24	1·16	2·01	0·67	0·64
CaO . .	5·09	2·01	7·15	10·43	12·65	14·37
MgO . .	—	0·77	1·09	0·99	—	1·98

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[1] *Zeitschr. d. Ver. Deutsch. Ing.*, 1894, p. 185.

[2] *Loc. cit.*

The earlier experiments for extracting metallic zinc from these ores failed on account of their high percentage of iron and manganese, by which the retorts were destroyed. On the other hand, the treatment of the raw ores for iron was rendered difficult by the amount of zinc present. An American, Samuel Wetherill, was the first to succeed in treating these ores by employing them for the production of zinc white by means of special furnaces designed by himself. The residues, rich in iron and manganese, which were thus obtained, and which only retain a small quantity of zinc, proved to be a suitable material for the production of spiegeleisen, which is at present extracted from them. Wetherill reduces the zinc oxide of the ores in furnaces, lying upon a grate designed by himself, or upon a bed of anthracite resting upon the latter, zinc being thus produced which is burnt to zinc oxide immediately upon its production, by the air and the carbon dioxide contained in the products of combustion. The process is only successful when pure oxidised ores are employed, such as exist in the above-named ore mixtures, when the fuel used is a pure coal burning without the formation of smoke or soot, such as is found in Pennsylvanian anthracite, and when the Wetherill grate with blast in the ashpit is made use of. The zinc oxide intermixed with the products of combustion is cooled down and collected in bags after the zinc has been completely burnt, and particles of coal and ashes have been separated from it, whilst the permanent gases evolved escape through the pores of the bags. As regards the construction of the furnace, and of the cooling and condensing arrangements, the furnace is similarly constructed in all the above-mentioned works, whilst the cooling and condensing plants only differ in unessential details.

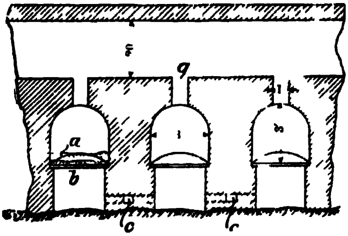

FIG. 165

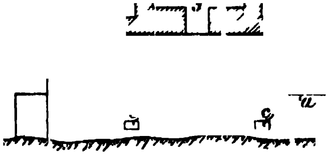

FIG. 166

The Wetherill furnace, represented in Figs. 165 and 166, consists of an arched chamber provided with doors at either end. Inside it there is a grate, *a*, consisting of a plate of cast-iron 1·4 inches thick, pierced with conical holes (100 holes to the square foot), the upper smaller end being 0 4 inch in diameter, whilst the lower larger diameter amounts to 1 inch; the grate is supported upon cast-iron bearers. Owing to the conical shape of the holes they are prevented from becoming stopped up. Underneath the grate there is a closed ashpit, *b*, into which air is introduced by means of lateral flues, *c*. The air is forced by means of a fan into a flue running underneath the ashpits of a whole series of furnaces, as shown in Figs. 167 and 168, in which *C* shows the flue running underneath the furnace *a*. From this main flue small flues ascend in the brickwork between the individual furnaces, and these are connected at their upper ends by means of small horizontal flues with the ashpit. These horizontal flues, *c* (in Figs. 165 and 166), can be closed by means of dampers, so as to enable the blast to be cut off from any particular furnace, if the charge in it has been worked off, or for repairs. In the arch above the furnace there are flues through which the gases, vapours and flue dust escape. With smaller furnaces there is only one flue, *q* (in Figs 165 and 166) to each furnace. Larger furnaces (Fig. 167) have two flues. The gases and vapours pass through these flues either directly into a main flue, *h* (Figs. 165 and 166), or as at the Lehigh

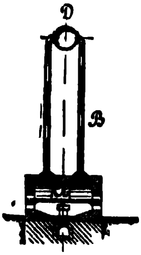

FIG 167.

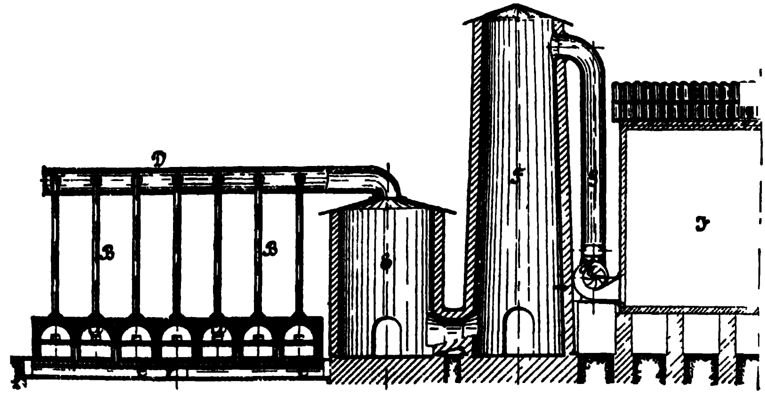

FIG. 168

Zinc Works (Figs. 167 and 168), first into vertical iron pipes, *B*, and then into a main flue, *D*. The individual furnaces are united to form blocks, which contain up to 34 furnaces (see Fig. 168). The furnaces are either single or double, according as each furnace extends through the whole width of the block or not. The width of the furnaces at the grate is 3 feet; the length of the single furnaces amounts to 5 feet 5 inches, that of the double furnace to 15 feet. The height of the crown of the arch above the hearth is 3 feet. The area of the flue in the arch is about 1 square foot. The doors at the short ends of the furnaces are set in arches 12 inches high and 32 inches wide. The gases pass through the collecting flues into two towers one after the other, in which, on the one hand, any unburnt zinc vapour is completely burnt to zinc oxide, whilst, on the other hand, any particles of ash or fuel carried off with them, are deposited. The towers used at the Lehigh Works are shown in Fig. 168.[1] The current of gases and dust passes through the tube *D* into the tower *E*, being drawn in by means of a fan, erected behind the second tower.

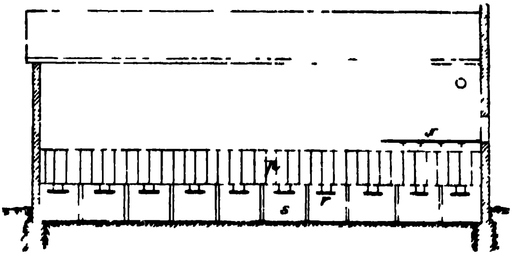

Fig. 169.

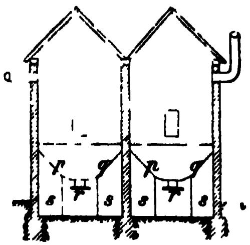

Fig. 170

It then escapes from the bottom of the first tower into the tower *F*, 69 feet high and 79 feet in maximum circumference, which it also traverses from below upwards. Many of the towers are said to also contain partition walls. From these towers the gas current passes into cooling chambers. A fan is arranged between the last tower and the cooling chamber, by means of which the current is driven into the latter. In Fig. 168, *G* is the outlet from the last tower, *H* is the fan, and *J* the cooling chamber. At many works the current is divided between two cooling chambers, which it traverses lengthways. In these chambers the current of gas and dust is cooled down to such an extent that the zinc oxide and gas can be separated from one another in bags of cotton or twill without injury to the latter. The construction of the cooling chambers used at the Lehigh Zinc Works is shown in Figs. 169 and 170.[2] They are 98 feet 6 inches long, 20 feet wide, and 42 feet 6 inches high up to the base to the roof, their walls consisting of polished woodwork, whilst the roof is made

[1] Durre, *loc. cit.* [2] Strecker, *Jahrb. d. K. K. Montanlehranstalten*, 27, 1879.

of corrugated iron, and the floor, which is formed of sheets of iron, *p* and *q*, sloping towards each other, rests upon supporting walls *s*. In order to remove the oxide of zinc deposited in these cooling chambers, there are shoots, *r*, in the bottom, provided with sliding doors; *x* is a drying floor made of sheet iron upon which the zinc oxide, collected in the cooling chambers, is dried. From the cooling chambers the gas current enters the chambers in which the zinc oxide is caught, the so-called bag chambers. In these the current is distributed through a system of horizontal pipes running near the roof. At distances of 3 feet apart vertical branches descend which have also prolongations upwards. To these there are attached bags or hose 30 to 36 feet long and about 2 feet in diameter, made of strong cotton which hang down vertically. They are either open below, or else several such sacks are connected together at the bottom in the form of a U. The zinc oxide collects inside these bags, whilst the permanent gases escape through the meshes of the cloth and thus into the open air. The arrangement of these bag chambers at the Lehigh Works is shown in Figs. 171 and 172.[1] *K* is the tube which conveys the current of gas from the cooling chamber, *J*, into the bag chamber. It opens into the main pipe, *L*, 6 feet wide, from which the lateral branches, *M*, open out. *N* are the bags attached to these branches. The topmost portion of the bags has also been made of wire netting for a length of some 6 feet, in order to avoid any injury to the upper portion of the bag by the gases, which are still hot. The open bottom ends of the bags rest either upon the floor or open into casks, in which the zinc white is collected by beating the bags. There are altogether 708 of these bags at the Lehigh Works.

The ore and anthracite are employed crushed to pea size. The grate is first covered with a bed of anthracite, varying in weight between 165 and 200 pounds, according to the area of the grate. The blast is then turned on, and as soon as the layer of coal is thoroughly ignited, a mixture of ore and anthracite is piled upon it. A single furnace is charged with 250 to 300 lbs. of ore and a double furnace with 480 to 520 lbs., anthracite to the amount of 40 per cent. of the weight of the ore being mixed with it. When the furnaces are being regularly worked they remain sufficiently hot after the residues from the treatment of a charge have been removed, to ignite the next charge. The air, entering through the holes in the grate, burns the anthracite, producing carbon dioxide. This, on its ascent through the layer of anthracite, is partly reduced to carbon monoxide by means of which gas, as also of the carbon of the intermixed coal, the oxide of zinc is reduced to metal The vapours of the latter are converted into zinc oxide by the action of the oxygen in the excess of air, as also, after partial cooling, by the carbon dioxide contained in the current of gas, and this zinc oxide is carried off by the gaseous current, passes with the latter through the above-described apparatus, and is finally caught in the bags already described The time occupied in working a charge depends upon the size of the furnace At Bethlehem, with a single furnace treating 300 lbs of ore per charge, it occupies 4 hours, at the Passaic Works, with a charge of 250 lbs, 6 hours One workman per shift is required for every 4 single furnaces His duties, in addition to charging and emptying out the furnace, are to keep the charge sufficiently open for the blast to pass through it, and to see that the temperature is main-

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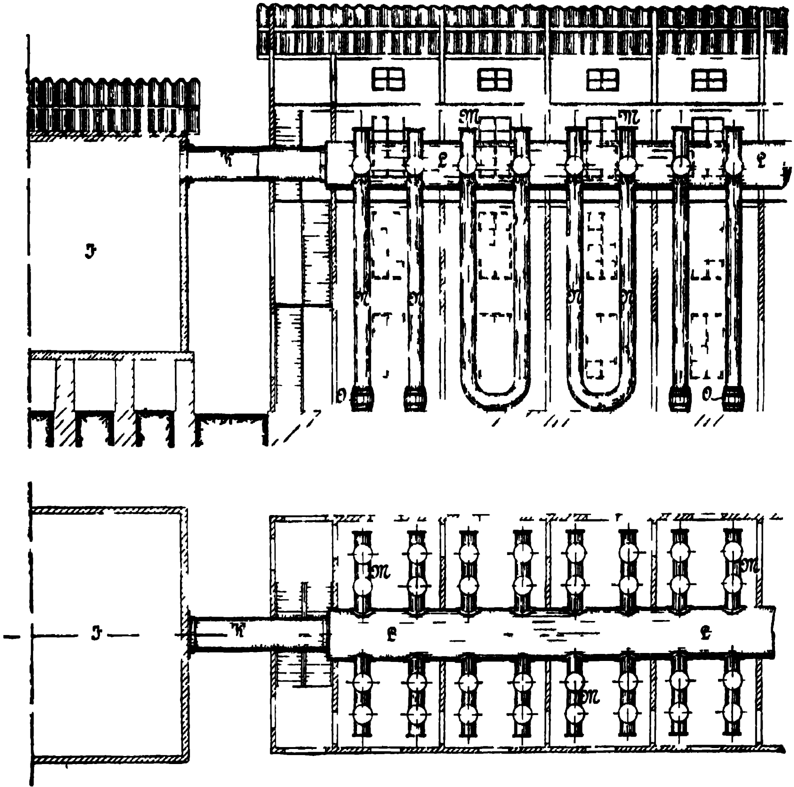
[1] Dürre, *loc. cit.*



FIGS 171 and 172

tained. The residues remaining on the grate generally contain from 2½ to 4 per cent. of zinc, so that the loss of zinc varies from 10 to 20 per cent. of the percentage present in the ore. The proportion of zinc retained by the residues cannot be diminished either by increasing the quantity of coal or by leaving the charge for a longer time in the furnace. It depends solely upon the depth of the layer of ore and is less the thinner the charge is spread out upon the grate. For instance, in a series of experiments at the New Jersey Works,[1] when the depth of the charge above the grate amounted to between 5 and 8 inches, and the charge was left from 5 to 6 hours in the furnace, the percentage of zinc in the residues was from 1·20 to 4 per cent., whilst when the charge was spread in a layer 12 to 18 inches thick and left for 13½ to 28 hours, it amounted to 8 to 10 per cent. The residues partly form sintered blocks 2 inches in thickness, partly small pieces and dust. In addition to the constituents of the ore that remain behind, they also contain the ashes (15 to 20 per cent.) of the anthracite, as well as lime, which is in many cases added. According to Dürre, their chemical composition varies between the following limits:—[2]

	Per cent.
Silica	18 to 28
Ferric oxide	29 „ 36
Alumina	2 „ 9
Manganous oxide	10 „ 20
Zinc oxide	3 „ 15
Lime	8 „ 16
Magnesia	1 „ 4

On account of their richness in iron and manganese they are smelted for spiegeleisen. The zinc oxide is collected in the abovementioned bags, whilst impure zinc oxide to the extent of 2 to 3 per cent. of the total quantity produced is deposited in the flues, pipes, towers and cooling chambers. The latter is removed from time to time, generally once a week, and is either sent into the market as inferior zinc white or is returned with the ores to the Wetherill furnaces, or is smelted for metallic zinc in retorts. The zinc white deposited in the bags is removed from them by shaking and beating from time to time, generally at intervals of from 2 to 4 hours, and is collected into barrels. If it is damp, it must first be dried upon the drying floor of the cooling chambers and then sifted in a cylindrical sieve, the screening surface consisting of closely-woven linen. At some works, as at Bethlehem, the dried and sifted zinc white, after the casks have been filled, is compressed by means of a press attached to the side or cross-walls of the building, and the cask is then again filled up. The zinc white is sometimes also pressed first in ordinary sacks, and then packed in casks.

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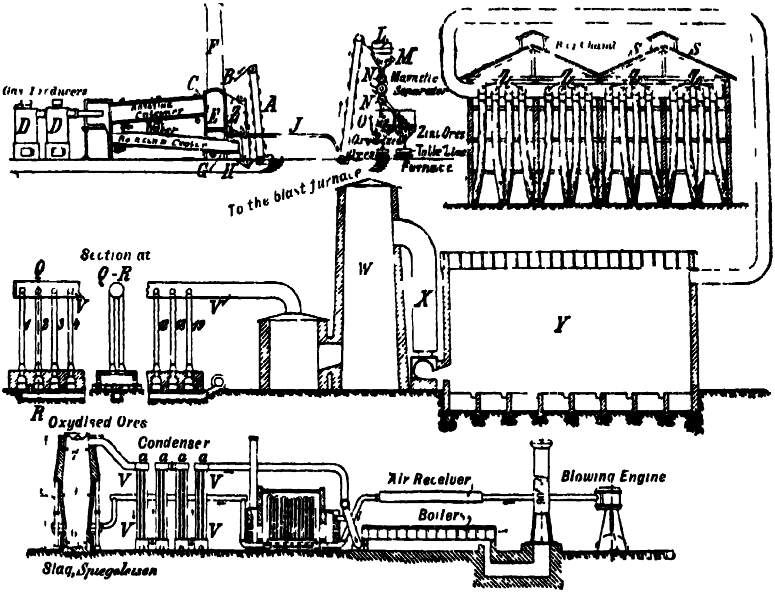
[1] Strecker, *op. cit.*, p. 344.

[2] *Loc. cit.*

At the works in South Bethlehem, the ore first undergoes a reducing calcination in order to convert the iron into magnetic oxide, and is then divided into portions, poor and rich in iron respectively, by means of a magnetic separator. The portion poor in iron which contains 46·38 per cent. of zinc, 3·76 per cent. of iron, and 6·68 per cent. of manganese, is smelted for spelter of a high degree of purity known as the Stirling brand, whilst the portion rich in iron, which contains 29·66 per cent. of oxide of zinc, 37·20 per cent. of iron, and 9·34 per cent. of manganese, is first treated for the production of zinc white, and then smelted for spiegeleisen. The reducing calcination is performed in a rotating calciner heated by gas shown in Fig. 173.[1]



FIGS. 173—177.

The ore is mixed with 20 per cent. of its weight of anthracite and then introduced into the rotating calciner, *C*, over the sloping surface,

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[1] V. Ehrenwerth, *Mining and Metallurgy at the Chicago Exhibition*, Vienna, 1895.

B, by means of the elevator, *A*. The furnace is heated by producer gas generated in Taylor gas producers, *D*. The ore escapes through the bottom end of the furnace heated to bright redness, whilst the products of combustion escape at the upper end into the stack, *F*. From the rotating furnace the ores enter the rotating cooler, *G*, through which a current of cool air passes, whilst water is allowed to run over the outside. The cool ore is raised by means of the elevator, *H*, into the hopper, *Z*, and carried by a blast through the pipe, *J*, into a second elevator, which raises it on to the sieve, *L*, upon which the unconsumed anthracite is retained. The ore that passes through the sieve is transferred to three magnetic separators, *N*, lying one below the other. The non-magnetic portion of the ores from each separator enters the hopper for zinc ores. The separator works with a current of 50 ampères and a tension of 80 volts, requiring 20 horse-power to drive it, and treating 40 tons of ore in 24 hours.

The construction of the furnace for the production of zinc white is shown in Figs. 174 to 176, the plant for collecting the zinc white in Fig. 177. The furnace grate is 10 feet long and 4 feet wide. Furnace and ashpits are provided at their short ends with doors, which are kept closed during the operation. From the arch of each furnace two vertical sheet-iron pipes lead into the main pipe, *V*; the latter opens into a cooling chamber which is connected to the cooling tower, *W*. From this tower the zinc oxide passes into the pipe *X*, and by means of a fan is forced into the cooling chamber *Y*, which communicates with the bag chamber *S*. After the grate has been covered with a layer of anthracite, this is ignited, and then a layer of mixed ore and anthracite 4·7 to 7 inches deep is spread over it. The blast is then introduced, and at the end of 6 hours 83 per cent. of the zinc of the ore is converted into zinc white. A small portion of the latter is collected in the cooling chamber, the greater portion in the bags of the bag chamber. For 100 parts of franklinite 56 parts of coal are employed for admixture and 46 as fuel, the product of the above quantity of franklinite being 24·5 parts of zinc white, containing 99·87 per cent. of oxide of zinc, and 1·5 parts of impure zinc white, containing 99·34 per cent. of oxide of zinc, together with 66·22 parts of residues. The latter are treated for spiegleisen and zinc oxide. Their composition is as follows:—

	Per cent.
Zinc oxide	6·1
Iron	38·98
Manganese	10·83
Silica	19·89
Phosphorus	0·026

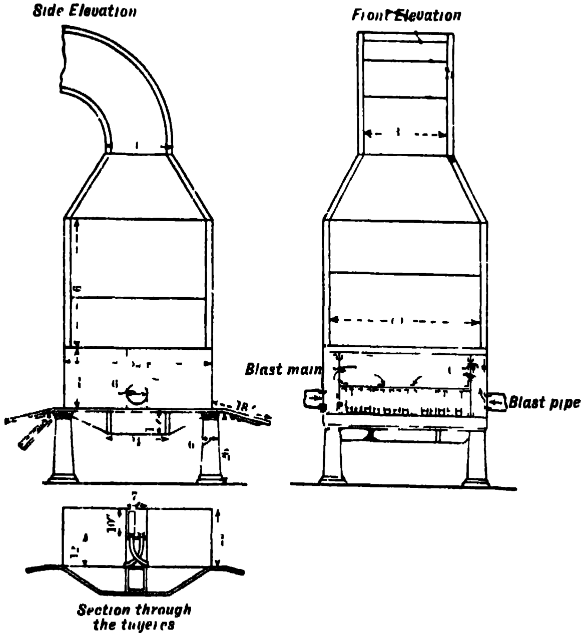
The residues are smelted in a blast furnace 35 feet high, with hot blast heated to 480° C.; the vapours of zinc escape from this furnace at so high a temperature that they cannot condense in the upper portions of the latter. The vapours and gases pass from the blast furnace as shown in Fig. 177 into an arrangement, *V*, consisting of vertical pipes in which zinc white and metallic zinc are deposited; the gases are then used as fuel for the generation of steam and for heating the blast. To each furnace there are 2 of these condensers for collecting zinc and zinc oxide, which are used alternately, so, that the working of the furnace need not be interrupted whilst they are being cleaned out; 66·22 parts of residues (=100 parts of franklinite) yield 31·72 parts of spiegeleisen, 2·33 parts of impure zinc oxide containing 74·16 per cent. of oxide of zinc, and 57·80 parts of slag, 10 tons of spiegeleisen being produced every 24 hours. For the production of 100 tons of spiegeleisen, 208·6 tons of residues, 114·7 of limestone, and 208·6 of anthracite are required.

Zinc white is extensively used in the United States for paint. It has the disadvantage, as compared with the zinc white produced in Europe by the combustion of zinc, that it becomes slightly yellow in time. Zinc white is produced from zinc blende in the same way as it is from ores containing franklinite. If this blende is not dead roasted, the zinc oxide will contain some sulphate. At Bergenport the charge consists of 645 lbs. of calcined blende, and 300 lbs. of anthracite. Gray oxide of zinc has also been produced in this way in Europe. In Swansea, England, and in Belgium, calamine and the dressed residues from distillation vessels have been similarly treated for zinc oxide. If the ores contain galena, sulphate of lead and oxide of lead are also formed, these bodies likewise passing into the zinc white.

Preparation of Mixtures of Oxide of Zinc, Sulphate of Lead and Oxide of Lead

At various works the zinc is removed from lead ores containing zinc by reduction of zinc oxide and oxidation of the escaping zinc vapours. The zinc oxide thus formed, which always contains considerable quantities of lead sulphate and lead oxide, is collected and sold as a paint. If the ores contain silver, a portion of the silver always passes off with the oxides. This process is carried out in reverberatory furnaces and in hearths. It is in use at Joplin, Missouri, and at Cannon City, Colorado, and is known in these places as the

Bartlett process. At Joplin, Jaspar County, Missouri,[1] the ore consists of blende containing galena with 70 to 73 per cent. of lead. It is treated in double hearths cooled by air and water, the construction of which is shown in Figs. 178 to 180, with the addition of 2½ per cent. of lime, the first products being lead, zinciferous lead, fume and slag. The hearth rests upon cast-iron columns, so that its lower portion is cooled by air. The hearth space is divided by a hollow cast-iron block, lying on the bottom, into two portions, each of which forms a separate hearth, and can be worked independently of the other. This partition forms the back wall common to both furnaces, and has an opening in the lower portion, through which it fills with molten lead. Upon it lies a hollow cast-iron water box in which water circulates, and above this is an iron air box divided lengthways into two portions in which air circulates. Through both divisions of the air main the



FIGS. 178—180

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[1] Davey, *Trans. Am. Inst. Min. Eng.*, vol. xviii., p. 674; Clerc, *Eng. Mng. Journ.*, July 4, 1896; Ramsay, *Scientific American*, Supplement, May 14, No 593, 1887; *Trans. Am. Inst. Min. Eng.*, February, 1889; J. R. Holibaugh, *Lead and Zinc Mining in Missouri and Kansas*, New York, 1895.

last passes into a row of copper tuyeres, 7 for each division, which ass through the water box and convey the blast, heated in the air ox, into the hearth. By means of the blast a portion of the galena s converted into lead sulphate and lead oxide, which bodies combine vith the undecomposed sulphide of lead to form metallic lead and ulphur dioxide. A portion of the lead is volatilised and oxidised by he blast; a portion of the lead sulphide is also volatilised and converted by the blast into sulphate. The sulphide of zinc is first converted into zinc oxide, which is reduced by the fuel, the blast converting the zinc vapour again into oxide. The lead and zinc fume is cooled, and then collected in woollen bags, forming a gray powder. By burning out the carbonaceous substances, particles of soot and coal, contained in it, it is converted into white crusts, which are smelted with the slag obtained in smelting the galena, in low blast furnaces with coke at a very high temperature. An additional row of tuyeres is provided in the upper portion of the blast furnace for the oxidation of the volatilised lead and zinc. Lead, slag and fume are thus produced. The last-named is first cooled, and then collected in bags, and forms a white product, saleable as paint. Its composition is shown in the following analysis :—

	I	II
$PbSO_4$	65·46	65·00
PbO	25·85	25·89
ZnO	5·95	6·03
Fe_2O_3 .	0·03	0·02
CaO .	0·02	0·02
CO_2 .	1·53	2·00
SO_2 .	0·04	—
H_2O .	0·69	0·85
Insoluble	0·08	0·08

In the above described hearth 13½ tons of ore are treated in 24 hours with a fuel consumption of 13½ tons of coal.

At Cannon City, in Colorado, a similar process is in use b means of which the lead, silver and copper contained in the ore are finally concentrated in a matte. At Freiberg calcined zinciferous lead and silver ores were formerly smelted in reverberatory furnaces with coke, whereby the reduced zinc was volatilised and collected as zinc gray. In consequence, however, of the volatilisation of lead and silver this process has been given up.

The Production of Zinc Vitriol

At the Herzog Julius Works, at Goslar, and at the Sophia Works, near Langelsheim, zinc vitriol is produced from the lead ores of

Rammelsberg, which contain considerable quantities of zinc blende. These ores consist of:—

	Per Cent.
Galena	9 to 12
Zinc blende	27·5 to 30
Copper pyrites	1 to 1·69
Iron pyrites	11 „ 16
Gangue	44 „ 47

The gangue consists chiefly of barytes. The ores are calcined three times in heaps, by which a portion of the sulphide of zinc is converted into sulphate. The latter is more especially contained in the small ore, which is therefore removed after each fire. The first fire lasts for 6 or 7 months, heaps of 500 tons being treated; the second and third fires are given in calcining houses, the heaps being left uncovered. Each heap contains above 500 tons of ore. The second fire lasts 6 to 8 weeks; the third, 4 to 6 weeks. The small ore separated after the various fires contains the zinc partly in the form of neutral zinc sulphate, partly as a basic sulphate, which is not soluble in water. It has the following average composition:—

	Per Cent.
Ag	0·015
CuO	1·34
PbO	14·44
ZnO	19·12
Fe_2O_3	22·95
SO_3	15·95
S	0·60
Insoluble residue, alkaline earths, CO_2, H_2O, traces of Mn	8·505

In order to remove the neutral zinc sulphate, the small ore is systematically leached with water and waste solutions, and after being dried in reverberatory furnaces is smelted for lead, together with the lump ore from the third fire, in blast furnaces. The small ore is leached in horizontal cylindrical drums driven by machine power. The ends of these drums are made of cast iron, the sides of wrought iron. Their length is 3 feet 11 inches and their diameter 3 feet 3 inches, and they will contain from 1 to 1¼ tons of ore. The ore is leached four times, the two first times with the unsaturated solution from a previous operation, the two last times with hot water. The drums make 25 revolutions per minute. The first leaching lasts 15, the second 25, the third 10, and the fourth 5 minutes. The first solution of 50°B. and the second of 20°B. are mixed so as to form a lye of 30°B., clarified, freed from iron and sulphate of lime, and then evaporated down to the crystallising point, when the zinc vitriol is allowed to crystallise out. The solutions are clarified first in wooden troughs 30 inches broad and 22 inches deep, and then in brick tanks lined with cement, 10 feet long, 4 feet 3 inches broad, and 3 feet 3 inches deep. These tanks are provided with a wooden grating, upon which there is a layer of the richest small ore. The solution is thus further concentrated by being allowed to filter through this layer. The clarifying of the solution consists in heating it for 24 hours to a temperature of 80° to 90°C., in pans made of sheet lead 0·5 inch thick, 13 feet long, 10 feet broad and 2 feet deep, which stand upon a cast-iron plate, and are surrounded with a brick wall one brick in thickness. The solution is then transferred to wooden boxes lined with sheet lead, 10 feet long, 7 feet 3 inches broad and 3 feet 3 inches deep, for a period up to 10 days. The iron is converted by the heating into a basic sulphate, and separates out together with the sulphate of lime and other difficultly soluble bodies, in the tanks. About half a ton of coal is required for the clarifying of 255 cubic feet of solution of 30°B. The solution thus purified is evaporated in pans similar to those used for clarifying, down to 50°B., and is then run out into cooling vats made of wood lined with sheet lead 0·12 inch thick, in which the zinc vitriol is allowed to crystallise out for 6 to 8 days. The concentration of the solution from 30° to 50°B. lasts about 20 hours, the consumption of coal being from 17 to 18 cwts. The cooling tanks are 32 feet 9 inches long, 5 feet broad, 16 inches deep at the sides, and 20 inches in the centre. The crystallised vitriol is dried. It has the following composition :—

	Per Cent.
ZnO	25·45
MnO	2·32
FeO	0·47
SO_3	29·54
CuO	trace
H_2O	41·67

The presence of manganese gives it a pale pink colour. The mother liquor is pumped back into the evaporating pans until it becomes too impure.

A portion of the zinc vitriol is worked up into calcined vitriol. For this purpose it is heated in copper vessels, which have lately been replaced by wrought-iron pans, 3 feet 3 inches deep and 4 feet in maximum diameter, until it melts in its water of crystallisation, when it is stirred continually for 3 or 4 hours. The impurities that separate out are then skimmed off, and it is finally ladled into wooden tanks, in which it is stirred with wooden paddles until it solidifies to a fine grained mass. It is then sifted and packed in barrels. At the Sophia Works 266 tons of crystallised vitriol produced 232 tons of calcined vitriol, with a consumption of 2,750 cubic feet of cord-wood.

CADMIUM

PHYSICAL PROPERTIES

CADMIUM has a white colour with a bluish tinge; its structure is dense, its fracture hackly. It crystallises in the forms of the cubical system. It is soft and ductile, and can be both beaten out into thin foil and drawn into wire. It is intermediate between tin and gold in hardness and tenacity.

Its specific gravity when cast is said to be 8·604, when hammered 8·694.

When bent it "cries" like tin.

Its melting point is 316° C. according to Wood, 320° C. according to Rudberg, and 355° C. according to Wagner. Its boiling point is given as 720° C. by Becquerel, and as 860° C. by Deville and Troost. Its vapour is orange-yellow and burns in the air, forming brown cadmic oxide.

An addition of zinc renders cadmium brittle.

It has the property of lowering the melting points of certain of its alloys. Thus Rose's metal, composed of 2 parts of bismuth, 1 part tin and 1 part lead, melting at 93¾° C., has its melting point brought down to 75° C. by the addition of 8 to 10 per cent. of cadmium. An alloy containing 8 parts lead, 15 parts bismuth, 4 parts tin and 3 parts cadmium becomes pasty at 60° C. and quite fluid at 70° C.[1]

The melting point of soft solder, containing 37 per cent. of lead and 63 per cent. of tin, is reduced to 136° C. by the addition of 8 per cent. of cadmium, and to 132° C. by the addition of 25 per cent.[2]

THE CHEMICAL PROPERTIES OF CADMIUM AND OF ITS COMPOUNDS THAT ARE OF IMPORTANCE IN ITS EXTRACTION

When heated in the air to its boiling point, cadmium burns to an amorphous brown oxide, infusible at a white heat. It only decomposes water when water vapour and cadmium vapour are allowed to interact at a red heat. At lower temperatures it only decomposes water in the presence of acids. It is soluble in hydrochloric, nitric and sulphuric acids. Zinc precipitates it from its solutions. Sulphuretted hydrogen precipitates it from moderately acid solutions as a sulphide of various shades of yellow. According to Niederländer,[1] cadmium sulphide of a pale yellow colour is produced from solutions of the chloride or the sulphate when the current of sulphuretted hydrogen is interrupted after half the metal has been precipitated, when the gas is allowed to come into contact as little as possible with the precipitate, and when the latter is washed with hot water. The dark yellow sulphide is produced by complete precipitation with constant stirring and heating of the precipitate during the whole period of the operation. A 10 per cent. solution is best suited to the production of both the pale and the dark yellow sulphide.

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[1] Lipowitz, *Dingler*, vol. 158, p. 376.

[2] Hauer, *Dingler*, vol. 177, p. 154.

Orange-yellow cadmium sulphide is produced when sulphuretted hydrogen is passed into a nearly boiling 2 per cent. solution of the chloride containing 5 per cent. of free hydrochloric acid, the precipitate being constantly stirred throughout the precipitation.

Cadmium oxide is reduced to metal by carbon and carbon monoxide in the same way as zinc, the temperature of reduction being however lower than in the case of the latter metal. As cadmium also volatilises at a lower temperature than zinc, these metals can be separated in the dry way without any special difficulty.

Cadmium hydrate is soluble in ammonia, but insoluble in excess of the carbonates of potash, soda or ammonia

Cadmium alloys with many of the heavy metals; its alloys with gold, platinum and copper are brittle, those with lead and tin ductile; its alloys with silver and mercury are ductile only in certain proportions.

Zinc is rendered brittle and finely granular by a considerable admixture of cadmium.

SOURCES OF CADMIUM

Cadmium occurs in nature as sulphide, CdS, with 77·6 per cent. of cadmium, the mineral being known as Greenockite. It occurs in such small quantities and is so rare (*e.g.* at Bishoptown in Scotland) that it cannot be regarded as a source of cadmium. It occurs, however, in small quantity in most zinc ores, especially in blende and calamine, for example, in amounts of 2 to 5 per cent. in Spanish calamines, of 2 to 6 per cent. in the radiated blende of Przibram, of 1·136 per cent.

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[1] *Chemiker Zeitung*, 1893, No. 82.

in blende from Nussières, and of 0·13 to 0·21 per cent. in Belgian blendes. It also occurs in the zinc ores of Upper Silesia, the Harz, Freiberg, Derbyshire and Cumberland. When these ores are treated in the dry way, the cadmium accumulates in those bye-products that pass over first on distillation, namely, zinc fume, *poussière*, and flue-dust. The zinc itself also often contains cadmium. These bodies, of which poussière from Belgium may contain as much as 30 per cent. of cadmium, form the sources from which this metal is obtained.

Cadmium is used for the production of easily fusible alloys, of amalgam used for stopping teeth, of cadmium sulphide which serves as a yellow oil colour, of cadmium iodide and bromide for photographic and of the sulphate for medicinal purposes On account of its limited applications, and of its low price due thereto, only small quantities of cadmium are ever extracted.

THE EXTRACTION OF CADMIUM

Cadmium may be obtained by both dry and wet methods. no attempts have yet been made to produce it electrolytically.

It is, as a rule, obtained at present in the dry way. The methods that have been proposed for its wet extraction have not as yet been put into practice.

Extraction in the Dry Way

The extraction of cadmium in the dry way depends upon the property of cadmium oxide of being reducible to metallic cadmium vapour by the action of carbon and carbon monoxide, at a temperature below that at which zinc oxide is reducible to metal, and upon the property of metallic cadmium of volatilising at a lower temperature than metallic zinc.

If a mixture of zinc and cadmium oxide is accordingly exposed to the action of carbon in retorts at a comparatively low temperature, about redness, cadmium is reduced first and vaporised, and can therefore be condensed in receivers and thus separated from the zinc. When a mixture of zinc oxide, zinc, cadmium oxide and cadmium, with a comparatively low percentage of cadmium, such as forms the usual material for the extraction of cadmium, is reduced by carbon, a pulverulent mass is obtained in the receiver, consisting of cadmium oxide, cadmium, zinc oxide and zinc, considerably richer in cadmium than was the original mixture. Cadmium can then be extracted from this mixture either direct or after another further enrichment by a repetition of the process of distillation.

The original material is, as already stated, obtained in the process of zinc distillation, the easily reducible and volatile cadmium mixed with zinc-dust and zinc oxide, being deposited in the cones attached to the adapters for zinc distillation, or in the first dust chambers connected with these.

The extraction of cadmium was formerly conducted as follows in the Upper Silesian zinc works:—

The material was furnished by the so-called *first poussière*, that is to say the flue-dust or zinc-dust collected during the first 3 or 4 hours of the 'distillation, in the sheet-iron cones attached to the adapters; it was mixed with small coke in the proportion of 23 cubic feet of coke-dust to 2 cwt. of zinc-dust, and distilled at a red heat in ordinary muffles with adapters. The zinc was thus in part collected in the adapters, whilst the dust enriched in its cadmium contents was caught in the attached cones. A charge took 12 hours to work off, and after every three charges the residues rich in zinc were removed from the muffles.

The dust rich in cadmium thus obtained was mixed with charcoal and distilled at a red heat in small cylindrical cast-iron retorts, provided with sheet-iron adapters, and which were heated in the stack of the calamine calciners. The cadmium collected in the adapter, which was closed by a wooden plug. A charge was treated in 12 hours, and after three charges had been worked off, the residues were removed. The cadmium was remelted and cast into thin rods.

At present *first poussière* is no longer produced at the majority of the works in Upper Silesia. Cadmium is now extracted from the oxides deposited in the first portion of the dust-chambers, such as form the continuation of Kleeman's and Dagner's adapters. These oxides contain over 1 per cent. of cadmium; they are mixed with a suitable proportion of coal, and are distilled at a low red heat in the retorts that are used for zinc extraction, long sheet-iron cones being used as adapters; cadmium collects in the latter intermixed with cadmium oxide, zinc and zinc oxide. The material so enriched is mixed with charcoal and distilled in small cast-iron or clay retorts; the former, used at Lipine, are furnished with long conical sheet-iron adapters. The latter have no adapters, but are set at an angle, so that the cadimum collects in the front portion, whence it can be drawn off through a tap-hole and cast into moulds. Cadmium collects in the adapters of the cast-iron retorts in the solid state. It is transferred to a ladle, covered with a layer of the oxides cleaned out from the retorts, then with a layer of tallow and melted. After fusion it is allowed to cool down somewhat, and is then cast in moulds made of paper rolled up so as to produce rods weighing 2 to 3 ounces each.

The cadmium collected in the clay retorts is tapped out into ladles and poured direct into cast-iron moulds made in two halves, which also produce it in the form of rods.

At Lipine the dust-catchers connected with the Kleeman adapters in which latter a good deal of cadmium is volatilised, yield flue-dust containing at the outside 3 per cent. of cadmium. Dust containing 5 to 6 per cent. of cadmium may be obtained by using globular sheet-iron receivers attached to the adapters: these are taken off at the expiration of 1½ to 2 hours, and the dust that clings to the sides is shaken out.

The flue-dust so obtained is next treated in an ordinary zinc muffle, provided with a taper conical sheet-iron adapter about 3 feet long The charge for the muffle consists of 55 lbs. of flue-dust and 44 lbs of *cinder*. Distillation takes about 22 hours, and the working about 2 hours. Flue-dust is deposited on the inside of the adapter, considerably enriched in cadmium, but containing widely varying amounts of that metal. It is further treated in cast-iron retorts, 2 inches high in the clear, and 6·7 inches wide, the metal being about 1 inch thick; these are provided with a tapering conical sheet-iron adapter, about 16 inches in length. The charge for a retort consists of 3 to 3½ lbs. of flue-dust, and 11 to 13 lbs. of clean and fine-grained *cinder*. Cadmium in the form of drops and cadmium oxide are deposited inside the adapter. this mixture is transferred to a small cast-iron ladle and heated under a layer of tallow, the molten cadmium being then cast into rods. The residues from the muffles and retorts are returned to a subsequent charge.

At the Paul Works in Upper Silesia, flue-dust collected from the flues connected with the Dagner adapter is used as a source of cadmium. It contains 3 to 4 per cent. of cadmium, and is distilled, as at Lipine, at a red heat for 24 hours in ordinary zinc muffles provided with a conical sheet-iron adapter. Flue-dust with 20 per cent. of cadmium is thus obtained, which is mixed with *cinder* and distilled in a cylindrical clay retort about 10 inches in diameter and 4 feet long, the operation lasting 24 hours. The charge for a retort is 33 lbs. The retort has no adapter, and inclines towards the front of the furnace; the cadmium collects in this portion of the retort, and is tapped through a small hole into a ladle from which it is poured direct into moulds. The residues from the retorts are added to the charges for zinc distillation.

At Engis in Belgium[1] zinc-dust, averaging 1·5 to 1·6 per cent. of cadmium, is mixed with coal-dust and treated in Belgian furnaces carrying three rows of small cast-iron tubes with cast-iron adapters and sheet-iron nozzles, the product being dust with 6 per cent. of cadmium. In 12 hours 2 cwt. of dust are treated in 11 tubes, yielding 28 to 32 lbs. of enriched dust. The latter is distilled again in the same plant, producing metallic cadmium, 28 to 32 lbs. being treated in 12 hours in four tubes. The cadmium collects in the adapters, whence it is drawn off at intervals of 1 hour, so that it shall be as free from zinc and iron as possible. It is then cast into moulds. The residues from the distillation contain 0·30 per cent. of cadmium; of the cadmium contents of the original dust, 30·12 per cent. is saved, 21·17 per cent. is left in the residues and 48·71 per cent. is volatilised. Three grades of cadmium are produced; the purest kind, which is readily bent, amounts to about one-half of the total; the next contains 75 per cent. of cadmium and can be bent with difficulty but yet without breaking, whilst the poorest quality contains only 40 per cent. of cadmium and is very brittle. The inferior qualities are purified by fractional distillation. According to R. Wagner a sample of Silesian cadmium had the following composition:—

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[1] Stadler, *Journ. f. Pract. Chem.*, 1864, vol. 91, p. 359; *Dingler*, vol. 172, p. 286.

Cd	94·86
Zn	4·96
Fe	0·23

Sp. gr. 8·528. Melting point 368° C.

Extraction of Cadmium in the Wet Way

Wet processes have been proposed for extracting cadmium both from zinc fume and from metallic zinc, containing cadmium,[1] but have not yet come into use.

The older suggestions depend upon the fact that when the above substances are treated with hydrochloric acid, zinc will dissolve before cadmium, whilst the latter metal can be thrown down from its solutions by the former. The substances are to be treated with hydrochloric acid in such quantity that a portion of the zinc remains undissolved and can thus precipitate any cadmium that may have gone into solution; any lead present will also be found in the residue. The latter is then treated with hydrochloric acid until a little cadmium has gone into solution, thus showing that all the zinc has been dissolved out. The cadmium is thrown down from the solution by means of rods of zinc. The mixture of lead and cadmium is then subjected to distillation. The solution is to be neutralised with zinc fume, and the zinc thrown down from it as a hydrate by milk of lime.

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[1] *Berg. und Hutt. Ztg.*, 1862, p. 305.

Another method for obtaining cadmium sulphide or oxide has been proposed by Kosmann[1] for the flue-dust of the zinc reduction and blend calcination furnaces of Upper Silesia.

The flue-dust from the zinc furnaces, the composition of which has been given on pages 183 and 184 is to be treated with neutral ammonium carbonate, which dissolves the zinc, whilst the cadmium remains as insoluble carbonate. The solution is heated, when ammonia and a part of the carbon dioxide are driven off, whilst basic zinc carbonate is formed which can be converted into zinc oxide by heating. The residue is heated to convert the carbonate of lead present into oxide, and is then digested with solution of lead acetate, which dissolves the oxide of lead. Carbon dioxide is passed into the solution, precipitating the lead as white lead. The residue that was left, containing the cadmium, either as oxide or as carbonate, may be treated with dilute sulphuric acid to dissolve the cadmium, which may be thrown down as sulphide by means of sulphuretted hydrogen. If cadmium oxide is to be produced, the residue is treated with nitric acid, the solution of cadmium nitrate is evaporated and the salt heated, when brown cadmium oxide is left behind.

This process has never come into use.

Flue-dust obtained in calcining blende from Upper Silesia also contains cadmium; it is partly soluble and partly insoluble in water. The composition of two samples from the Silesia and Godulla works respectively is shown by the subjoined analyses[2]:—

I. Flue-dust from the Silesia Works.

	Soluble.	Insoluble.	Insoluble per cent.
ZnO	17·144	7·192	16·809
PbO	—	6·285	14·690
CdO	0·874	1·147	2·680
TlO	0·006	–	—
FeO	1·896		—
MnO	1·332	0·042(Mn_3O_4)	0·098
Fe_2O_3	2·900	9·043	21·135
Al_2O_3		3·115	7·280
CaO	0·714	0·478	1·117
MgO	0·168	0·440	1·028
As_2O_3	–	0·401	0·937
P_2O_5	—	0·263	0·614
SO_3	20·430	6·612	15·453
H_2O	11·400	—	—
Residue	–	7·765	18·146
	56·864	42·786	99·997
	99·650		

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[1] *Preuss. Minist. Zeitschr.*, 1883, p.,238.

[2] *Berg. und Hütt. Ztg.*, 1862, p. 505.

II. FLUE-DUST FROM THE GODULLA WORKS.

	Soluble.	Insoluble.	Insoluble per cent.
ZnO	10·991	9·532	15·430
PbO	—	8·980	14·486
CdO	1·120	1·518	2·449
TlO	0·006	—	—
FeO	1·676	- -	—
MnO	0·481	1·591(Mn_3O_4)	2·566
Fe_2O_3	2·940	15·928	25·696
Al_2O_3	1·191	4·601	7·423
CaO	0·464	1·071	1·640
MgO	1·337	0·858	1·065
As_2O_3	-	1·280	2·066
P_2O_5	-	0·394	0·604
SO_3	13·320	9·061	15·101
H_2O	4·850	—	—
Residue	-	6·804	10·976
	38·376	61·618	99·502
	99·994		

Kosmann proposes to treat this flue-dust first with water and then with sulphuric acid: the cadmium is dissolved as sulphate, in part in the aqueous solution, in part by the acid. The solutions are mixed and heated, to precipitate iron and calcium sulphate. The solution is then diluted with water, and the cadmium precipitated as sulphide. Arsenic is precipitated as sulphide along with it, and is said to improve its colour. If cadmium oxide is required, the sulphide is to be roasted, the arsenic being volatilised as trioxide and condensed.

This process also has not come into use.

Extraction of Cadmium by Electrolytic Methods

Borchers[1] was able to precipitate cadmium from its solutions in laboratory experiments, using a current of 6 to 14 ampères per square foot; it may therefore be obtained in form fit for use more readily than zinc.

Brand[2] also obtained favourable results in experiments on the purification of cadmium contaminated with zinc and other metals by the help of the galvanic current; the tension in the bath was low, and the metal obtained quite pure. He used for his anodes plates of impure cast cadmium, containing cadmium 88·7 per cent., zinc 8·55 per cent., lead 1·45 per cent., copper 1·35 per cent., with smaller amounts of antimony, arsenic, bismuth and iron; his electrolyte was a solution of cadmium sulphate with 5 per cent. of free sulphuric acid and 0·8 lb. cadmium to the gallon. With electrodes 2 inches apart, and a current intensity of 12·8 ampères, the tension in the bath was only 0·042 volt, because the solution of the zinc, which remained in the electrolyte, introduced a considerable amount of electric energy into the circuit. The tension increased to 0·048 volt, as soon as the solution contained together with 5 per cent. of sulphuric acid, 0·464 lb. of zinc, and 0·04 lb. of cadmium to the gallon.

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[1] *Elektro-metallurgie*, 1895, p. 298.

[2] Dammer, *Chem. Technol.*, vol. ii., pp. 33, 687.

MERCURY

PHYSICAL PROPERTIES

MERCURY or quicksilver is the only metal fluid at ordinary temperatures. It has a silver-white colour with a slight bluish tinge, and a perfect metallic lustre. According to Melsens, it is transparent in thin layers, showing a blue colour with a somewhat violet tinge. According to Cavendish, it solidifies at −39·38 C.; according to Hutchins, at −39·44 C., and according to Mallet, at −38·85 C. It contracts upon solidification, and forms a white, very ductile and malleable mass, which is readily cut with a knife. It raises blisters on the human skin on contact, just like red-hot metal. Its specific gravity, when fluid, at 0° C., is 13·5959 according to Regnault, 13·595 according to Kopp, and 13·589 according to Biot and Arago. The specific gravity of solid mercury is 14·1932. It crystallises in the forms of the cubical system. The specific heat of solid mercury between −78° and −40° C. is 0·0247, that of the fluid metal, between 0° and 100° C., is 0·0333. Its electrical conductivity according to Matthiesen at 22·8° C. is 1·63, silver at 0° being taken as 100. Its thermal conductivity according to Calvert and Johnson is 677, compared to that of silver taken as 1,000. Mercury is volatile to a slight extent at ordinary temperatures, and according to Merget even below −44° C. This may be proved by suspending gold leaf above a vessel containing mercury, when it will become coated at ordinary temperatures with a white layer of amalgam. The boiling point of mercury, according to Dulong and Petit, is 360°, according to Regnault, 357·25° C.; it is converted into a colourless vapour, the density of which is given as between 6·7 and 7·03. The rapidity with which mercury volatilises on boiling depends to a great extent upon its purity. It is mainly diminished by lead and zinc, and on the contrary increased by platinum. Millon showed that in the same time and under otherwise similar conditions, thirteen times as much pure mercury was volatilised as of mercury containing $\frac{1}{10,000}$ of lead. Platinum increases the rapidity of evaporation if digested for one or two days with mercury at a temperature of 50° to 80° C. Iridium, gold, silver, copper, nickel, cadmium and arsenic have no influence upon the rapidity of evaporation.

At ordinary temperature the cohesion of pure mercury considerably surpasses its adhesion to lighter bodies. When therefore it is allowed to run over an inclined surface of paper or glass, it forms spherical masses or globules. When it is impure, it leaves a film upon the above-named surfaces, and does not run in spherical globules but in pear-shaped ones. When agitated with air, it then leaves a black powder; by violent agitation of mercury with various fluids, as also by rubbing it up with certain bodies such as sugar and grease, it is converted into a fine dark gray powder Vapours of mercury have a most injurious effect upon the animal system. In all operations in which mercury vapours are evolved, it is therefore necessary to take especial precautions to protect the persons engaged therein.

CHEMICAL PROPERTIES OF MERCURY AND OF ITS COMPOUNDS, WHICH ARE OF IMPORTANCE FOR THE EXTRACTION OF THE METAL

Pure mercury is unchanged in dry air at ordinary temperatures; neither is it affected by long-continued agitation with air, oxygen, nitrous oxide, nitrous acid or carbon dioxide. In damp air, however, it gradually becomes coated with a thin film of mercurous oxide (Hg_2O). Impure mercury becomes coated with a film of oxide even in dry air. If mercury is heated for a considerable time up to 350° C. in the air, it oxidises to mercuric oxide (HgO), which according to Pelouze is crystalline. This gradually decomposes in the sunlight into mercury and oxygen. When heated it is rapidly decomposed, the mercury being volatilised. When again cooled down, it is partly re-converted into mercuric oxide. Mercury, distilled by heating the latter, is therefore rendered impure by oxide, and is accordingly somewhat pasty.

Mercuric oxide produced in the wet way by precipitation from mercuric salts has a bright orange-yellow colour, which according to Pelouze is an amorphous modification of mercuric oxide.

Dilute sulphuric acid has no action upon mercury. Concentrated boiling sulphuric acid dissolves it with the evolution of sulphur dioxide. When mercury in excess is present, the mercurous salt is produced; with excess of sulphuric acid, on the other hand, the mercuric salt is formed. Hydrochloric acid does not attack mercury. Nitric acid, even when dilute, dissolves mercury, forming a nitrate, the mercurous salt being formed in the presence of an excess of mercury and when cold acid is employed, but the mercuric salt, when heated with an excess of acid or when strong acid is used.

Mercurous salts, as also mercuric sulphate and nitrate, are decomposed by water into soluble acid and insoluble basic salts. Mercurous salts when heated decompose, producing mercuric salts and metallic mercury.

Aqua regia dissolves mercury with comparative readiness, mercuric chloride ($HgCl_2$) being formed. Chlorine in the gaseous condition or in solution in water, attacks mercury at ordinary temperatures, mercurous chloride being formed, and gray pulverulent mercury being produced. Boiling mercury burns in chlorine gas with a yellowish-red flame, forming mercurous and mercuric chlorides.

Mercuric chloride, so-called corrosive sublimate, is prepared by dissolving mercury in aqua regia, by dissolving mercuric oxide in hydrochloric acid or by the addition of common salt to mercuric sulphate. Mercurous chloride, known as calomel, is produced by treating mercuric chloride with mercury or by precipitating mercurous salts by means of hydrochloric acid. Both chlorides have a white colour and are volatilised on heating, mercurous chloride subliming without previous fusion. Mercuric chloride is readily soluble in water; mercurous chloride is soluble neither in water nor in dilute acids.

Sulphide of mercury (HgS), the most important compound of mercury for the metallurgist, occurring native as cinnabar, can be produced as an amorphous black mass by rubbing together flowers of sulphur and mercury and by gently heating the mixture of the two bodies. If this mass is heated to its melting point, mercuric sulphide volatilises, and may be condensed in the form of a brownish red crystalline sublimate. This on grinding, becomes scarlet and forms artificial cinnabar. When gently heated, air being excluded, it is readily re-converted into black amorphous mercuric sulphide, but if heated more strongly, it again sublimes as red sulphide. Native cinnabar begins to darken at 200° C., and to volatilise; at 350° it volatilises to a very great extent, but for its complete volatilisation, a low red heat, 500° to 600° C., is required. With excess of air, it burns at 350° C. with a blue flame of sulphur, forming sulphur dioxide, metallic mercury separating out and volatilising. The red sulphide of mercury darkens under the action of light, and after a considerable time it becomes black in consequence of the separation of free mercury. The specific gravity of artificial cinnabar is 8·124 according to Boullay, whilst the specific gravity of its vapour according to Mitscherlich is 5·51. It is therefore assumed that upon the volatilisation of sulphide of mercury, partial dissociation takes place. Mercuric sulphide can be produced in the wet way by the action of alkaline polysulphides upon mercury, or by the action of sulphuretted hydrogen or alkaline sulphides upon solutions of mercuric salts. In these processes, black mercuric sulphide is obtained If the latter is brought into contact with alkaline polysulphides it passes into red mercuric sulphide slowly in the cold, but rapidly on heating. This phenomenon, which has been utilised for the production of artificial cinnabar in the wet way, has been explained by supposing that black mercuric sulphide dissolves in solutions of alkaline polysulphides, and crystallises out of the solution in the form of the red sulphide. Mercuric sulphide is not attacked by hot nitric acid. Aqua regia dissolves it rapidly with th formation of sulphuric acid and the separation of sulphur. Mercuric sulphide forms double sulphides with the sulphides of the alkalies. The potassium salt for instance has the formula $HgSK_2S + xH_2O$; it contains variable quantities of water according to the temperature and the concentration of the solution. A portion of these double sulphides is soluble in water in the presence of caustic alkalies, but at a certain degree of dilution is decomposed again into its constituents. Mercuric sulphide forms peculiar double compounds with mercury and copper salts. For instance, by passing sulphuretted hydrogen into a solution of mercuric chloride, a white deposit of the composition $2HgS+HgCl_2$ is first formed, which becomes yellow and finally black under the continued action of sulphuretted hydrogen. Sulphide of mercury is soluble in solutions of sodio-cuprous chloride. Mercuric sulphide is soluble in bromine. According to Regnault, mercuric sulphide is partly decomposed by water vapour, sulphuretted hydrogen being formed and mercury separating out together with a black sublimate. When sulphide of mercury is heated with carbon, it is partly decomposed according to Berthier, carbon bisulphide being formed, and mercury separating out. When heated with other metals which possess a greater affinity for sulphur than mercury, for example with iron, tin or antimony, the mercury is liberated in the form of vapour, whilst the sulphur combines with the respective metals. Copper and zinc are said by Heumann to decompose cinnabar at the boiling point of water, or at ordinary temperatures under pressure. When mercuric sulphide is heated with lime, the mercury separates out and volatilises, sulphide and sulphate of calcium being produced as shown by the following equation :—

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

Alloys of Mercury

Mercury combines directly with most metals in all proportions, forming so-called amalgams; with gold, silver, zinc, tin, cadmium, lead and bismuth it amalgamates readily; copper amalgamates easily when finely divided, but with difficulty in the massive state; arsenic, antimony and platinum amalgamate with difficulty, iron, nickel and cobalt not at all directly. The amalgams of the last named three metals can only be produced indirectly under certain conditions, for example by means of electrolysis when a solution of a mercuric salt is used for the electrolyte and one of the above named metals as cathode, or when sodium amalgam is brought in contact with solutions of these metals, or when the metals are brought in contact with solutions of mercury. These amalgams are very unstable and decompose readily, iron amalgam for instance when violently agitated. When mercury amalgams are heated to the boiling point ot mercury, the latter separates in the form of vapour, whilst the respective metals are set free.

ORES OF MERCURY

Mercury occurs in nature in but relatively few minerals. The only ore of mercury which occurs in considerable quantities in nature, and which alone forms the object of an independent extraction of mercury, is cinnabar. Native mercury often occurs with this ore, but only in very subordinate quantities. The other true ores of mercury are of no importance for the extraction of that metal. In addition to the true ores of mercury, mercury occurs isomorphously intermixed with other minerals, especially with fahlores, and in very minute quantities in zinc blendes. In the fahlores, in some localities it is contained in such quantity that these are worth treating for mercury.

Native Mercury

This generally occurs in deposits of cinnabar as a decomposition product of that mineral, and, therefore, generally near the outcrop of such deposits. In these it is generally found in the form of small disseminated globules or in filiform masses. It is rare to find the individual globules so large that the mercury can be collected from them. Considerable quantities of native mercury disseminated through serpentine have been found for instance at the outcrops of various deposits of cinnabar in California (Sonoma Mine, Rattlesnake Mine, Wall Street Mine). It is said to occur in a decomposed granite, unaccompanied by cinnabar, in the neighbourhood of Limoges, especially at Mélinot near St. Lô, and also, accompanied by calomel, in the strata upon which the town of Montpellier stands. It occurs alloyed with silver in the form of *native amalgam* which contains 26·5 to 35 per cent. of mercury, and is looked upon as a silver ore. This mineral has been found at Moschellandsberg in the Rhine Provinces, at Rosenau in Hungary, Allemant in France, and Argueros in the province of Coquimbo in Chili.

Cinnabar or Cinnabarite (HgS)

This mineral contains 86·2 per cent. of mercury, and is the only ore which is regularly worked for mercury, on which account it deserves fuller consideration. It but rarely occurs in large masses, but generally disseminated or intermixed with metallic oxides, earths bituminous substances or iron pyrites; of the metallic minerals, iron pyrites is the most frequent, followed by arsenical and antimoniacal compounds, and ores of gold, copper and zinc. As regards its geological distribution, it may be noticed that it occurs in strata of almost all ages from Archaean crystalline schists to Quaternary deposits. It is also found in deposits from eruptive rocks and from sulphurous springs of volcanic origin, as also at times in the eruptive rocks themselves. It is still being deposited in the fumaroles of Sulphur Bank, near Clear Lake, in California.

Cinnabar is dimorphous. In addition to the red crystalline variety, there is also a black variety possessing no crystalline structure and a lower specific gravity than red cinnabar, which is known as meta-cinnabarite. Cinnabar intermixed with bituminous bodies, which give it a dark red to black colour, is known as hepatic cinnabar. Idrialite is a mixture of cinnabar with idrialine (C_3H_2), occurring at Idria. Coralline ore is a mixture of cinnabar, bituminous matters and about 60 per cent. of calcium phosphate.

Cinnabar occurs at relatively few places in the world in sufficient quantity to be worked for the extraction of mercury. In Europe the most important localities which furnish the largest quantities of mercury are Almaden, in Spain; Idria, in Carniola; and Nikitowka, in the South of Russia.

At Almaden, on the northern slopes of the Sierra Morena between Badajoz and Ciudad Real, cinnabar occurs together with native mercury in an area 10 miles long and 6 miles broad, in Silurian and Devonian strata, consisting of slates, quartzites, sandstones, and small quantities of limestone, forming three almost vertical tabular deposits about 600 feet in length and 12 to 25 feet wide. In these deposits it occurs both in masses and disseminated. The contents of mercury of the different grades of ores vary from 0·75 up to 25·05 per cent.; it is said to average 8 to 9 per cent. In the year 1893, the production of mercury was 7·82 per cent. of the weight of the ores, and in 1894 8·19 per cent. These deposits were known to Theophrastus, as early as 300 B.C., and they are still to-day the most important mercury deposits in Europe.

At Idria, in Austro-Hungary, cinnabar, hepatic ore and coralline ore occur with native mercury in irregular deposits in Triassic strata. The deposits are partly of the nature of a stockwork, partly contact veins between limestone and dolomite, the various grades of ore containing from 0·2 to 30 per cent. of mercury, the average of the ores being from from 0·5 to 0·8 per cent. This deposit was known in the year 1490, and is, after Almaden, the most important in Europe.

At Nikitowka, a station on the Kursk-Charkoff-Azov railway line, in the district of Bachmut of the government of Eekaterinoslav in the South of Russia, cinnabar occurs impregnating sandstone strata of carboniferous age, having a thickness of 46 feet. The average proportion of mercury contained in this important deposit is given as 0·6 per cent. As is shown by old exhausted spoil heaps, this deposit has been worked in ancient and as yet undetermined times. Operations were recommenced only in the year 1886, and at present ores are produced in such quantities, that the mercury produced at the works attached to the mine not only supplies the demands of Russia, but is exported in considerable quantities. It may be considered as one of the most important deposits of the whole world. Regarded as a single works, it is the most important in Europe after Almaden and Idria. Among the other occurrences of cinnabar in Europe that possess a certain importance there may also be mentioned Vallalta, near Agorda, in the north-west of the state of Venice, where cinnabar occurs in the form of impregnations, whilst the ores are relatively poor; as also the deposits in the district of Monte Amiata in Tuscany, the principal mines being Salvena, Pian Castagnajo, and Diacoletto on the Siele, near Castellazzara. The works of Vallalta and those of Monte Amiata are still in operation, the mercury production of the latter being considerable. A recently discovered (1883) deposit of cinnabar of a certain importance is that in the Avala Hills, near Belgrade, in Servia, where mercury is also extracted. Deposits of mercury which were formerly of importance, but are now no longer worked either on account of the competition of other works, or on account of the exhaustion of the deposits, are those of Wolfstein and Moschellandsberg in the Bavarian Palatinate, of Horrowitz in Bohemia, of Volterra, Cerigliani and Ripa, near Serravezza, in the province of Lucca in Italy. Other deposits of subordinate importance in Europe are those of Mieres, Santander, Tobiscon and Purchena in Spain, of Neumarktel in the Santa Anna or Loibel Valley, of Littai (in veins of lead ore) in Carniola, of Balagna and Capo Corso in Corsica, of the Isère, Haute Vienne and the Sevennes in France, of Kongsberg in Norway, and Sala in Sweden.

In North America the most important deposits of cinnabar, the output from which exceeds that of Idria, and at one time exceeded that from Almaden, occur in California, in a zone of slates of the Cretaceous and Tertiary period, consisting of talcose, micaceous, clay and siliceous slates, serpentines, sandstones, limestones and dolomites, penetrated by numerous eruptive outbursts. This zone of slate is more or less strongly impregnated with cinnabar in various places, at some of which, especially where serpentine and sandstones are in contact, the proportion of mercury is a very high one, amounting to as much as 35 per cent. The ore occurs both as contact deposits and also disseminated in serpentine and in sandstones. At various places the cinnabar is accompanied by pyrites and bituminous substances. At others it occurs impregnating chalcedony which may then contain as much as 3 to 10 per cent. of mercury. The deposits occur in a district between the mouth of the Sacramento and Clear Lake upon the eastern slope of the chain of hills extending from San Francisco towards the south-east, known as New Almaden and New Idria, and the coast district about St. Louis Obispo and Santa Barbara. The most important occurrence which has furnished the largest quantity of mercury is that of New Almaden, near San José, lying to the south-east of the southern end of the bay of San Francisco; this deposit is however approaching exhaustion within a measurable period. The occurrence of Sulphur Bank to the east of Clear Lake is especially interesting on account of its association with an old geyser which is still throwing out boiling water with considerable quantities of gypsum, alkaline borates and sulphur. From the sides of some of the fissures in Sulphur Bank, ascending vapours deposit sulphur which is sometimes intimately mixed with cinnabar.

The ore of Sulphur Bank, which contains on the average 1·75 per cent. of mercury, is intermixed with sulphur, and was first worked for that substance.

The Californian cinnabar deposits were already known to the Indians, who used the cinnabar as a paint. Mercury was first extracted by Castellero in 1845. Whilst the deposits of Almaden and Idria seem to become richer in depth, the more important Californian deposits, especially those of New Almaden, seem to be approaching exhaustion. The average output of mercury from calcined Californian ores amounted in 1889 to between 1·088 and 2·295 per cent. according to Randall.[1] Cinnabar has also been found in the State of Texas. In Mexico, cinnabar is found near Capula and St. Romualdo in the State of Jalisco, at Pedemal, Carro and Guadalcazar in the State of St. Luis de Potosi, at Huitzuco in the State of Guerrero, and near Zacatecas. Many of these deposits were formerly worked, and some, especially at Guadalcazar, are still in operation. In South America a deposit of cinnabar, which was discovered in 1566, and was at one time of great importance, occurs in Peru in the district of Huancavelica. The ore occurs in Jurassic strata on the eastern slope of the Western Cordilleras, but is no longer worked at present. Other South American occurrences are those of Chonta, Cajamarca, and Santa Cruz in Peru, of the State of Tolima in Columbia, and at Andacallo in the Province of Coquimbo in Chili, La Cruz and Santo Tomé in the Argentine Republic, Paranagra, Santa Catherina, Santo Paulo and Oro Preto in Brazil.

In Asia the most important occurrence of cinnabar is in the Province of Kweitshow in Southern China. This is a very extensive deposit and traverses the above-named province from south-west to north-east. It is probably the richest deposit in the whole world. The most important district in which it is extracted is said to be that of Kaitshow in the neighbourhood of the capital, Kweiyang. The works were stopped in the year 1848, but are said to have been restarted recently. Cinnabar further occurs in Asia in the Province of Hoang Hai in China, at Senday in Japan, at Ildekansk in the district of Nertshinsk in Siberia, in Borneo, Sumatra, Java, and in the neighbourhood of Smyrna.

In Africa cinnabar has been found in various places in Algeria and Tunis.

In Australia it occurs at Cudgegong in New South Wales, Kilkivan in Queensland, and Omaperesee in New Zealand.

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[1] *Eng. Min. Journ.*, vol. 50, p. 265.

The other ores of mercury are of no importance for the extraction of that metal. Amongst them may be mentioned onofrite, a sulphoselenite of mercury, occurring at San Onofre in Mexico; coccinite, an iodide of mercury from Mexico; horn mercury or calomel, a native mercurous chloride, from Moschellandsberg, Avala, Idria and Almaden. Mercurial fahlore is a fahlore which contains certain quantities of mercuric sulphide. It may contain up to 18 per cent. of mercury. It occurs more especially in Hungary, at Altwasser, Rosenau, Szlana, Iglo and Göllnitz, where it contains considerable amounts of mercury, which is extracted from it as a bye-product, at the Stefans Works, near Göllnitz. Many varieties of zinc blende of the Rhine Provinces contain small quantities of mercuric sulphide.

Mercurial Furnace Products

Mercury is extracted not only from its ores, but also from certain furnace products which are obtained in the process of mercury extraction. These consist chiefly of so-called *soot* or "*stupp*,"[1] which consists of a mixture of finely divided mercury with soot, cinnabar, mercuric oxide, mercuric sulphate, other sulphates, quartz, &c., and of the residues obtained in treating this soot. In gold and silver extraction, amalgams are produced from which the mercury is recovered by distillation.

EXTRACTION OF MERCURY

EXTRACTION OF MERCURY FROM ORES

The extraction of mercury from its ores has up to the present been carried on in the dry way alone. Wet methods have repeatedly been proposed, but have not been able to make any headway, and there is for the present no likelihood of their being introduced. Neither has the electrolytic method of mercury extraction been adopted, although it would seem not to be entirely without favourable prospects.

The Extraction of Mercury in the Dry Way

The only ore from which mercury is extracted in practice is cinnabar. Ores containing only native mercury must be looked upon as exceptional; the mercury may be obtained from these by a simple distillation either in retorts or in shaft furnaces. Mercury is extracted from mercurial fahlores as an accessory product, when these ores are calcined. As may be gathered from the previously given chemical reactions of mercury, mercury may be extracted from cinnabar in various ways. Two methods are used upon a large scale. The one depends upon the fact that at a high temperature the oxygen of the air combines with the sulphur of mercuric sulphide, forming sulphur dioxide, whilst the mercury is set free in accordance with the equation :—

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[1] Derived from the Sclavonic word Stupa, meaning dust.

$$HgS + 2O = Hg + SO_2$$

The other depends upon heating the mercuric sulphide with lime when the sulphur combines with the calcium forming calcium sulphide and sulphate, whilst the mercury is liberated as shown by the following equation :—

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

Instead of lime, iron may be employed, as shown in the following reaction :—

$$HgS + Fe = FeS + Hg.$$

In every case, the above chemical reactions takes place at temperatures higher than the boiling point of mercury, so that the latter is separated in the gaseous form, and has to be condensed. In the former method the vapours of mercury are diluted by sulphur dioxide, nitrogen and oxygen, whilst in the latter case, where lime or iron is employed, they are in the concentrated condition, and are therefore more easily condensed. Hence the process of mercury extraction may be looked upon as a process of compound evaporation or distillation. According to the above, we have to distinguish :—

1. The extraction of mercury by heating cinnabar in the air;
2. The extraction of mercury by heating cinnabar with lime or iron, air being excluded.

As regards the choice of the most suitable process, the preference should, as a general rule, both for economic and for hygienic reasons, be given to the extraction of mercury by heating cinnabar in the air, rather than by the employment of lime or iron. Heating cinnabar in the air is a process that may be carried out either in shaft furnaces, reverberatory, or muffle furnaces. When shaft and reverberatory furnaces are used, large quantities of ore can be treated with a comparatively small consumption of fuel and labour; the process can also be so arranged that the workmen are not troubled by the mercurial vapours. On the other hand, the process is open to the objection that the mercurial vapours are diluted by sulphur dioxide, oxygen and nitrogen, and in the case of shaft and reverberatory furnaces, also by the products of combustion, and that the complete condensation of the mercury is therefore rather difficult, consequent losses of metal through incomplete condensation being accordingly unavoidable. The extraction of mercury by heating cinnabar with lime or iron must be performed in retorts. Concentrated mercurial vapours, which can readily be condensed, are thus obtained; but the process is open to the objection that the ores must first be crushed, that only small quantities can be treated, that the retorts last for only a comparatively short time, that the operation is attended with high costs for fuel and labour, and that the workmen are affected by the mercurial fumes when the retorts are emptied out. Although the output of mercury is somewhat higher than in the first-named process, it is nevertheless inferior to it on account of the high working costs, so that it is absolutely unsuitable for poor ores. The chief objection, that the workmen are attacked by the mercurial vapours, is of such paramount importance that the process should really not be carried on at all. It has therefore been given up at the majority of works, and has been replaced by the first-named process; its use can only be justified for the treatment of merely small quantities of ores containing a very high percentage of mercury.

EXTRACTION OF MERCURY BY HEATING CINNABAR IN THE AIR

This process must be regarded as a distillation process, although it might be looked upon as oxidising roasting, and therefore a process of combustion, if the metal to be extracted by it were not at the same time volatilised. It consists in heating cinnabar with an excess of air to such a high temperature that the affinity of the oxygen of the air for the sulphur of the mercuric sulphide becomes active, when the sulphur is oxidised to sulphur dioxide, the mercury separating out in the metallic form. A portion of the sulphur dioxide is converted into trioxide by contact action. The cinnabar is best heated to the requisite temperature, as will be shown presently, in shaft or reverberatory furnaces, the mercurial vapour being therefore diluted with various gaseous products, from which mixture it has to be separated, the difficulty being increased by the high temperature of the gases. As has been seen in the extraction of zinc, a metal which is also obtained by a distillation process, the condensation of the zinc vapours which are also diluted by other gases, forms the most difficult portion of the extraction. At a definite degree of dilution the zinc can no longer be obtained at all in the liquid state, but separates out in the pulverulent condition, a considerable quantity of which afterwards remains in the gases escaping from the condensers. The same occurs in the extraction of mercury, in which the condensation of the metal forms the most difficult portion of the process, in consequence of the dilution of its vapours by the above-named gases, of the high temperature to which the metal has been heated, and of the rapidity with which the current of gas has to pass through the condensing appliances. Nevertheless, the condensation of mercury vapours is more easily effected than that of zinc vapours, because the latter, owing to the low solidifying point of mercury (−39° C.), cannot separate out in the form of dust, but, when sufficiently cooled, necessarily forms a liquid, and because mercury can be caused to deposit without great difficulty on account of its high specific gravity, even from gases in which it occurs in a high state of dilution. It is, however, unavoidable that comparatively small quantities of mercury—a metal that is volatile at very low temperatures—should escape without being condensed. Even under the best conditions of working, the conversion of some mercury into the so-called "*stupp*" (mercurial *soot*) is unavoidable. The soot, which consists of a mixture of finely divided mercury, mercurial compounds, and sooty products of the dry distillation of the fuel and the bituminous constituents of the ores, together with its other mineral constituents, forms a deposit in the condensers. It contains up to 80 per cent. of mercury. Its formation is due, according to Patera, to the sulphates, formed when cinnabar is heated, and the chlorides, which were either contained in the ores or produced by the chlorides present in the ash, together with soot, tar and ammonia derived from organic matters, which substances envelop the particles of mercury as they condense, and prevent them from uniting. The greater portion of the mercury is recovered from the soot by processes to be described later on. Apart from the above-named objections, the extraction of mercury by heating cinnabar in the air forms one of the most difficult of metallurgical processes, requiring to be conducted with the greatest care, because considerable losses of metal are necessarily incurred, whilst diseases of the workmen engaged, due to mercurial poisoning, are practically unavoidable. Other difficulties are the penetration of the mercurial vapours into the brickwork of the furnace and condensers; the amount of mercury that remains in the distillation residues unless the utmost care is exercised; the comparatively small proportion of mercury in the ores that have to be treated; the acid character of the condensed water, owing to the sulphur dioxide and sulphur trioxide in the gases carrying the mercury, and its action upon the mercury, as also upon the metal of which the condensers are constructed; together with the further circumstance that mercury would form amalgams with such metals as are little or not at all affected by acid waters, and which would, therefore, otherwise be suitable for the construction of condensers, and the fact that the vapours must be extracted from the furnaces and condensers by means of fans in order to protect the workmen as far as possible. The losses of mercury, which formerly amounted to 50 per cent., and even more at some works, have recently, by a suitable construction of furnace and care in conducting the process, by lining the walls and floors of the condensers, and by suitably constructing the latter, and by proper regulation of the gaseous current, been reduced to 8 per cent., and even less of the mercury present in the ores. Considering the small proportion of mercury present in the ores, averaging 1 to 3 per cent., the unavoidable retention of small quantities of mercury in the residues of the latter, the unavoidable formation of soot, the action of acid waters upon the mercury, and the volatility of mercury at ordinary temperatures, the process of the extraction of mercury in its present stage of development must be looked upon as having been very well worked out when the loss is only from 6 to 8 per cent., and it no longer deserves to be considered as an imperfect or crude process as compared with other metallurgical operations. As regards mercurial poisoning, attempts have been made to protect workmen by the employment of suitably arranged fans in front of the condensers, so as to draw off all the gases which formerly escaped from the furnaces and condensers, and by carrying all the gases evolved into stacks, whereby a very marked diminution of mercurial poisoning has been attained. As, however, mercury is volatile even at ordinary temperatures, its vapour rising, according to Brame, up to the height of about 3 feet at 15° C., it will probably never be possible to avoid altogether the inhalation of small quantities of mercury, which are thus conveyed to the blood through the lungs. Mercury vapours produce disturbances of the nervous system, the digestion, the motor functions, and of the lungs, disease of the teeth, poverty of blood, scurvy and scrofula. When breathed in larger quantities, their effect is fatal. Among the prophylactic measures that have been recommended against mercurial poisoning are the following:—Cleanliness, open air, acid foods, and moderation in the use of alcohol. Melsens[1] recommends the employment of potassium iodide. This is said to render the insoluble mercurial compounds that have been taken into the system soluble, and cause their separation in the urine. A solution of potassic chlorate is used at New Almaden.

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[1] *Berg. und Hütt. Ztg.*, 1877, p. 236.

The plant in which the above process is carried out consists of various distillation appliances with condensing attachments. Distillation appliances may be heaps, stalls, reverberatory furnaces, shaft furnaces, and muffle furnaces. Distillation in covered heaps with alternate layers of fuel and ore, and the collection of the mercury in the upper layers and in the cover of the heap, a process which was for instance carried out a long while ago at Idria,[1] is a most imperfect process, owing to the volatilisation of mercury, to the retention of a comparatively large proportion of the metal in the ores, and to the penetration of the metal into the ground. At present it only possesses historical interest. For the same reasons stalls are unsuitable for the extraction of mercury. They are used exceptionally in the calcination of mercurial fahlores for the extraction of copper and silver. In this process the mercury is condensed as a bye-product in the upper layers of mineral, and is obtained by washing the latter. At the Stephans Works in Upper Hungary, mercurial fahlores are calcined in circular stalls, in heaps of 50 tons upon a bed of wood with a layer of charcoal above it. The calcination lasts 4 weeks. The mercury, extracted by washing the upper layers of ore, is purified by distillation.

Shaft and reverberatory furnaces are used both for lump ore and for small ore. Externally fired shaft furnaces for lump ore consist of an empty shaft, whilst for small ores the shaft is fitted with inclined slabs or plates. Formerly all of these furnaces used for lump ore were worked intermittently. At present, at most works, intermittently worked shaft furnaces of this type, in which small ores properly agglomerated, can also be treated, have been replaced by the much more economical continuous-acting furnaces. As a rule, externally fired shaft furnaces, working continuously, should be used for smalls that do not form dust, on account of the cheapness with which they can be worked. The ore slides down upon inclined slabs in the interior of the shaft, whilst the flame moves in the opposite direction from below upwards. Externally fired shaft furnaces would be used for lump ores if cheap uncarbonised fuels are available, whilst pure carbonised fuel, *e.g.*, charcoal, is dear. When cheap carbonised fuels are obtainable, the shaft furnace proper, in which the fuel is in direct contact with the substances to be heated, would be preferred to the continuous working shaft furnace externally fired, on account of the smaller formation of soot. Reverberatory furnaces, which were frequently employed, are inferior economically to externally fired shaft furnaces, as they require both more fuel and more labour than the latter. They are therefore only employed in those cases in which the shaft furnaces are not suitable, viz., in the case of small ore which forms much dust, of certain varieties of soot, and of lump ores that decrepitate in the shaft furnace.

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[1] Mitter, *Vortrag auf dem Bergmannstag zu Klagenfurt*, 1893.

Shaft furnaces proper, in which the ores are charged together with charcoal, have been in use for some time (Hähner furnace), but have recently received important improvements (Novak furnaces), and have, for example at Idria, replaced the modern externally fired furnaces for lump ores. In their construction they do not differ essentially from the externally fired shaft furnaces for lump ores, and are to be recommended on account of the small production of soot in those cases in which lump ores and cheap carbonised fuels, such as charcoal, are obtainable. These carbonised fuels form no soot, whereby the formation of mercurial soot (“*stupp*”) is lessened. Muffle furnaces were largely employed at one time, but have now been replaced at most works by reverberatory and shaft furnaces. The muffles were at first made of clay, but later iron has been used with advantage. These furnaces present the advantage that the mercurial vapours are not diluted by the products of combustion of the fuel, as occurs in the case of reverberatory and shaft furnaces, nor are they overheated, so that they can be readily condensed and therefore require less extensive condensing appliances. The extraction of mercury when the process is properly carried out is also somewhat higher in consequence of the diminished production of soot. On the other hand, these furnaces are liable to the objection of higher labour costs and of a high consumption of fuel, as also to the very serious objection that the workmen suffer more from mercury vapours than in the case of reverberatory and shaft furnaces. As, therefore, they are at least equalled in economic respect by the modern furnaces of the latter type, even when not surpassed by them, they have disappeared from most works, and, on account of the above reasons, their use should be discouraged.

Condensing Appliances

These ought to be manufactured of a substance which does not take up mercurial vapours, is a good conductor of heat, is capable of being moulded into the required shapes, and is able to resist the action of acid vapours and liquors, as also of the mercury itself. No one has as yet, however, succeeded in discovering a material answering to all these requirements. Of the substances used up to the present iron is the easiest to mould and the best conductor of heat, but does not resist the action of acid vapours for any length of time. Brickwork absorbs mercurial vapours, is a bad conductor of heat, and is attacked by acid liquors. Wood has sufficient resisting properties, but is a bad conductor of heat. Glass has not been found applicable by itself, but only in combination with wood. The most suitable material up to the present has been found to be stoneware. This is capable of resisting mercury and acids, and may be made so thin that its low conductivity for heat need not be taken into account. Stoneware is used in the form of pipes. In addition to stoneware, all the above-named substances are used, as also are vessels of burnt and glazed clay. Iron is protected by a coating of cement against the action of acid vapours and waters. The form which condensers assume is either that of a series of tubes or of chambers. Clay and stoneware are used in the former shape, iron and wood in both forms; brickwork and glass in the form of chambers. In many cases condensation in tubes is combined with condensation in chambers. The diameter of the tubes and the dimensions of the chambers must be confined within definite limits, as tubes which are too small interfere with the draught, whilst chambers which are too large have but little cooling effect upon the inner portion of the current of gases traversing them. By a suitable combination of tubes and chambers, or by chambers of different material, as also by means of brick chambers cooled by cast-iron boxes, through which water circulates, the losses of mercury by imperfect condensation have recently been brought down to a very small amount. A good draught in the furnaces and condensers, which is quite indispensable, may be obtained either by means of powerful stacks heated by separate fireplaces, or else by exhausting machinery of various kinds, such as water blast, Cagniardelle blower or fans. The draught must be such that the pressure of the current of gas in the furnace and condensers must be brought down below the pressure of the atmosphere, so as to prevent the mercurial vapours escaping from the apparatus. Recently draught produced by stacks has been replaced with advantage by the suction of powerful fans.

Mercury is transported in flasks of wrought-iron closed by a screw stopper. The weight of mercury in a full bottle amounts in Idria and Almaden to 76 lbs., in California to 76·5 lbs. In the smaller European works mercury is shipped, as was formerly done also at Idria, in bags of sheepskin containing 55 lbs.

The various distillation furnaces and the condensing appliances connected with them, the mode of conducting the process, and the economic results obtained, will now be considered in detail. For the sake of maintaining the proper sequence it is advisable to consider first the extraction of mercury in externally fired furnaces ("*flammöfen*"), shaft or reverberatory, then in shaft furnaces proper, and finally in muffle furnaces.

The Extraction of Mercury in Externally Fired Furnaces

Externally fired furnaces may be divided into those with a shaft-like laboratory chamber, so-called externally fired shaft furnaces, and reverberatory furnaces with a horizontally placed laboratory chamber, or true reverberatory furnaces. Externally fired shaft furnaces are generally used for the extraction of mercury, being employed for lump ores wherever raw fuels are cheap and carbonised fuels dear, and for small ore whenever it does not form too much dust. Reverberatory furnaces are used only for those ores which are not suitable for treatment in shaft furnaces, either on account of the large amount of dust in the case of small ore, or on account of their ready decrepitation in the case of lump ores.

Extraction of Mercury in Externally Fired Shaft Furnaces

These may be divided into furnaces working intermittently and furnaces working continuously. The former kind are still in use, but are far inferior to the latter as regards their economic results. In future, therefore, continuous working furnaces should as a rule be employed.

Extraction of Mercury in Shaft Furnaces Working Intermittently

These furnaces were formerly in use at Idria and at the Redington Works in California, but have been given up on account of their expense. They are still used upon a large scale at Almaden, in Spain. At New Almaden, in California, they were used for a considerable period, but have now been almost entirely given up, the last furnace of this kind still in existence there being worked only for a few weeks in the year. These furnaces can only be employed for ore fines, when these are charged in shallow vessels known as *casettes*, or when they have been agglomerated into bricks. The furnaces consist of shafts fired either internally or laterally. The condensing plant consists either of a series of flask-shaped clay pipes or of brick chambers. The fuel used must be uncarbonised, such as brushwood, wood or coal. The draught is produced by stacks, or better still by fans. The whole amount of ore to be treated is charged at one time into the furnace, and is heated by firing up until it continues to burn by itself owing to the heat developed by the oxidation of the sulphur in the cinnabar; after the fire has burnt out the furnace is left for some time to cool, when the distillation residues are removed, and a new charge introduced.

Furnaces Fired Internally

According to the system of condensers connected with these furnaces, they are distinguished into so-called Bustamente furnaces, the condensing appliances of which consist of a series of flask-shaped clay pipes, known as *aludels*, followed by chambers, and so-called Idrian furnaces, the condensers of which consist of a series of brick chambers. The furnaces are 20 to 30 feet in height, and circular or square in section, the diameter of the former being from 4 feet 3 inches to 6 feet 6 inches, and the side of the latter 10 feet. In the interior of the furnace there is a perforated arch which separates the fire-space from the distillation chamber above the arch. In order to diminish the pressure of the column of ore upon the side walls of the furnace, or in order to be able to place trays with ore fines conveniently in the furnace, perforated arches have also been introduced in the distillation chamber of the furnace.

The Bustamente Furnace or Aludel Furnace[1]

This furnace was designed in the year 1633 by a medical man, Lopez Saavedra Barba, in Huancavelica in Peru, and introduced in the year 1646 into Almaden, in Spain, by Bustamente, whose name it bears. In the latter place it has maintained itself up to the present in spite of many attacks. There are at Almaden 22 Bustamente furnaces, which furnish by far the greater portion of the mercury production of that place. In the middle of the eighteenth century, this furnace was introduced into Idria by Poll. Here, however, the aludels were soon replaced by brick chambers, whereby the Bustamente furnace was converted into an Idrian furnace.

The construction of the Bustamente furnace, together with the condensing appliances used at Almaden, is shown in Figs. 181 and 182. A pair of these furnaces is united to form a block. *S* is the cylindrical shaft, 20 to 26 feet high, the diameter of which for the smaller furnaces amounts to 4 feet 3 inches, and for the larger to 6 feet 6 inches. *Z* is a perforated brick arch, beneath which lies the fire-place *F*; above it is the distillation chamber. The upper part of the furnace is closed by a hemispherical arch, in which there is a charging door, *e*. The ores are first charged by means of the opening *O*, in the side wall of the furnace, which is bricked up before the commencement of the operation, and later on through the above-named charging door *e*, which is closed by a cover, luted with moist ashes. *H* is the firedoor through which the air required for oxidation also enters. *J* is a stack to carry off any products of combustion that do not ascend through the furnace; the greater part of these, however, ascend through openings in the brick arch and penetrate, together with an excess of air, through the column of ore lying upon the arch. The products of combustion, together with the

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[1] Kuss, *Mines et Usines d'Almaden: Annales des Mines*, 1878; *État actuel de l'Usine d'Almaden*, Ann. des Min., 1877; Escosura, *Historia del Tratamiento Metalurgico del Azogue en España*, Madrid, 1878; Gandolfi, *Les Mines et Usines d'Almaden*, *Rev. Univ. des Mines et de la Métall.*, 1889.

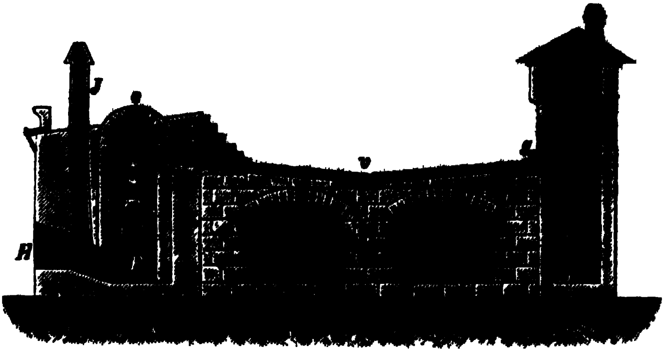

FIG 181

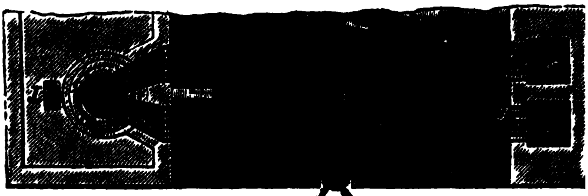

FIG 182.

mercurial vapours and sulphur acids evolved in the distillation chamber, pass through six openings, *K*, in the upper portion of the shaft, each of which is 12 inches high and 4 inches broad, into the condensers.

The condensing appliances consist of 12 strings or rows of aludels lying side by side, and of two chambers, with each of which six rows of aludels communicate. The aludels, one of which is shown in Fig. 183, consist of flask-shaped clay tubes, glazed on the outside, 16 inches to 18 inches long, 8 to 10 inches in diameter at the widest part, and 4¾ inches to 6 inches in diameter at the extremities. The object of the flask-like shape is to diminish the velocity of the gaseous current and thus to promote the condensation of mercury; 40 to 45 of these aludels are as shown in Fig. 184, connected together, so as to form a continuous tube. In order to prevent the escape of gas at the points of union, they are carefully luted. The rows of aludels lie parallel to each other in grooves in two surfaces sloping towards each other, so arranged that the first half of the row of aludels leads the gases and vapours downwards, and the second half conveys them upwards. The aludels that lie upon the descending half have each in the bottom of their widest portion an opening 0·08 to 0·16 inch in diameter, through which the mercury condensed in them escapes This opening is omitted in the aludels of the ascending half. The condensed mercury, part of which escapes from the above-mentioned holes, and part of which is emptied out from time to time from the aludels into the inclined grooves, runs into the inclined channel, *v* (Figs. 181 and 182), in which it collects, and flows from it into the pans, *s*, from which it escapes by means of the iron pipe, *f*, shown in Fig. 185, into a storehouse, where it is collected in graduated cast-iron pans, one of which is provided for each pair of furnaces in the block. From the row of aludels, the vapours and gases pass into condensing chambers, *w* (*h* in Fig. 185), built of brick, in which any mercury vapours not yet condensed are to be deposited. A partition wall, *g*, is introduced so as to lengthen the path of the vapours. Any gases not condensed escape into the stack, which is provided with a damper. The fuel used at Almaden was formerly brushwood, but is now coal.

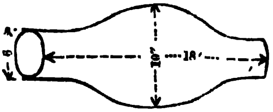

FIG. 183.

FIG. 184.

The charge for the larger furnaces is 13 tons of ore, for the smaller furnaces 8·7 tons. Together with this quantity 1·5 tons of small ore, moulded into bricks, known as *bolas*, are charged in each furnace.

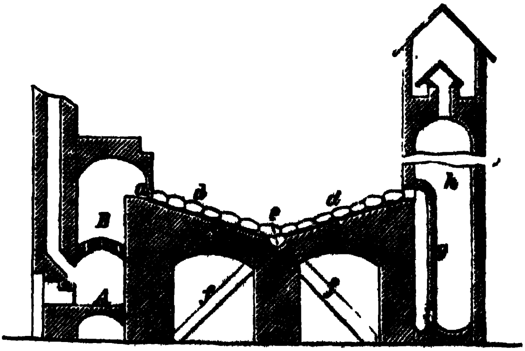

FIG. 185.

Four classes of ore are distinguished at Almaden, viz., *metal*, rich ore; *requiebro*, medium ore; *china*, poor ore; and *vacisco*, small ore. According to Escosura, the average consumption of these classes is as follows:—

	Metal.		Requiebro.		China.		Vacisco.	
	1	2	1	2	1	2	1	2
Cinnabar .	29·1	21·2	13·3	10·2	1·2	0·86	5·1	2·8
Iron pyrites . . .	2·2	2·0	2·0	1·9	2·1	2·8	12·3	1·5
Bituminous matter .	0·6	1·0	1·0	1·2	3·4	0·9	4·6	0·7
Gangue . . .	67·5	74·8	82·1	85·6	90·2	93·5	77·5	93·3
Total	99·4	99·0	98·4	98·9	98·9	98·06	99·5	98·3
Metallic mercury .	25·5	18·28	11·47	8·64	1·03	0·75	4·40	2·4

Before the ore is charged, the perforated arch is covered with a layer 2 feet deep of fragments of quartz or of poor lump ore (*solera pobre*), the pieces of which are such a size that the flame from the fuel can penetrate through them readily. Upon it ores of medium quality (*requiebro*) are charged, and upon this the poorer ores (*china*), which two kinds together amount to two-thirds of the total charge. Rich ore (*metal*) follows, upon which fragments of old aludels and blocks of fine ore (*vacisco*) and residues from soot treatment are placed; three men are occupied in charging, which takes 1½ to 2 hours. As soon as the whole charge has been introduced into the furnace, the two charging doors are closed, and the fuel in the firing chamber is ignited. Formerly, brushwood was used as fuel, but now coal is employed, which is burnt upon a grate. After 4 to 5 hours the first mercury shows in the front aludels. After firing from 10 to 12 hours, the column of ore has been heated sufficiently to be able to supply the heat required for the continuance of the process by the combustion of the sulphur in the cinnabar; firing is therefore discontinued. The air which serves to oxidise the sulphur is heated by its passage through the perforations of the arch and of the barren ore lying upon it to a temperature of 200° to 300° C. The ores burn for 43 or 44 hours, during which time mercury distils uninterruptedly. After the end of this second stage (*brasa*), the residues in the furnace are allowed to cool for some 18 hours, to promote which the doors of the fireplaces and the charging doors are opened. At the end of this time the distillation residues are drawn from the furnace, which occupies some 2 hours, after which the furnace is re-charged. Each campaign lasts upon the whole some 3 days of 24 hours: of this time, 10 hours are occupied in firing, 44 in the distillation, and 18 in the cooling. Formerly a charge consumed from 2·2 to 2·5 tons of fuel. Nowadays, owing to the employment of coal, a large furnace, taking a charge of 13 tons of lump ore and 1·5 tons of ore fines, requires 18 cwts. of coals, whilst a small furnace, taking 9 tons of lump ore and 1½ tons of fines, requires 14 cwts. of coal. As regards the temperature in the condensers, it has been found, according to Kuss, that the highest temperature in the first aludels is from 245° to 260° C., which is attained after 40 hours. In the tenth aludel from the furnace it reaches 105° C. at the end of 48 hours; in the midmost aludel of the row it amounts to 50° at the end of 52 hours; whilst in the last aludel of each row it rises to 29° at the end of 52 hours. The aludels which lie on the slope next to the furnace are cleaned out every month, those on the other slope every two months, to remove the mercury and soot contained in them. For this purpose the luting is removed and the aludels are held one by one vertically over the inclined gutters of the slope upon which the aludels lie, in order that the mercury contained in them may run into these gutters. The soot is then removed from them by means of brushes. It is collected in heaps, and treated in the manner to be described later on. The residues resulting from its treatment are moulded into blocks, together with ore fines, and treated in the furnace just described. Opinions vary as to the loss of mercury, which is given as between 4·41 and 25 per cent. According to L. de la Escosura,[1] Langer[2] calculates that the loss of quicksilver, when modern methods of assay are employed, averages 20 per cent. As already stated, the aludel furnace is in use nowhere else. It requires no proof that the intermittent process carried on in it is inferior to a continuous one. On the other hand, the condensing arrangement of rows of aludels followed by chambers, represents a principle which has been quite recently acknowledged as the correct one, although in modified form. The newest and best condensers have been arranged on this system in Idria, and consist of a series of stoneware pipes followed by wooden chambers.

The Idrian Furnace

This furnace is distinguished from the Bustamente furnace only by the construction of the condenser, which consists here not of aludels but of chambers lined with cement, six or eight of which are built on either side of the furnace. The gases and vapours, therefore, escape at both sides of the shaft. The Idrian furnace was designed in 1787 by von Leithner at Idria, and has been in use there, with various modifications, up to the year 1870. It was introduced in the year 1800 by Larrañaga into Almaden, and is still in use there, side by side with the Bustamente furnace. The original furnaces were rebuilt at Idria in 1825, either a pair or a single one forming a furnace block.[3] The double furnaces were called Franz furnaces; and quadruple furnaces, containing four in one block, Leopoldi furnaces. The construction of the modern Leopoldi furnaces at Idria is shown in Figs. 186 and 187, in which the condensing chambers on one side of the furnace only are shown. The furnace is square in plan, 10 feet in the side, and is furnished with two perforated brick arches. Upon the lower one, *a*, lump ores are placed, whilst the upper one serves to carry the clay or cast-iron pans in which the fine ore is charged. At one time, furnaces with three perforated arches in the shaft were employed. The fireplace is under the bottom brick arch, and is provided with a firegrate *c*, *w* being airflues; *h* are manholes for cleaning out the chambers; *x* are the escape flues, of which there are six on either side of the furnace; the bottom of the condensing chambers, *d*, slopes towards one side, in order to allow the condensed mercury to flow off into a gutter running along one side of the chambers, which conveys it into the magazine. From the last chamber the gas passes through the flues

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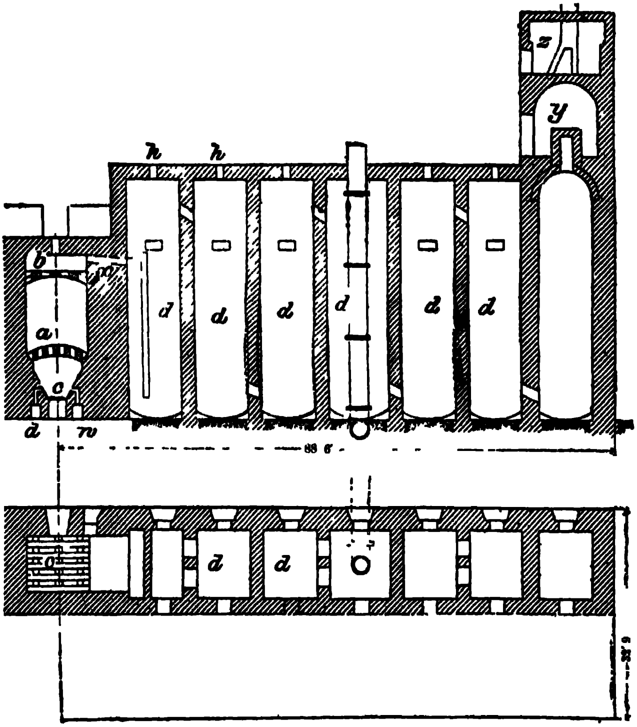
[1] *Op. cit.*, p. 448; Kuss, *op. cit.*

[2] *Beschreibung des Quecksilberbergwerkes Almaden. Berg. u. Hütt. Jahrb. d. Berg. Akad.*, 1879.

[3] Mitter, *loc. cit.*

y and *z* to the stack. The construction of the older form of double furnace with three arches is shown in Figs. 188 to 190, of which Fig. 190 shows the shaft on a somewhat larger scale than that of the other two figures. The lump ores are charged upon the bottom arch *x, x*; upon the middle one, *y, y*, ore of medium size is charged; and upon the top arch *z, z*, the pans with ore fines; *w* are the outlet flues, of which there are six on either side of the furnace, and *T* the condensing chambers connected with them. From the last and highest condensing chamber, *u*, the gases pass into the flue, *K*, leading to the stack. On either long side of the system of chambers there are gutters *r*, which collect the mercury from each chamber, (the bottom o which slopes towards the gutter), and which lead it to the magazine *V* and *W* are archways through which the air passes into the shaft o to the fuel. At one time only ore fines were treated in these furnaces



FIGS 186, 187

and were charged in pans, of which the furnace contained 1,800, with 44 lbs. of ore in each. This furnace was first fired for 10 to 12 hours, then it was left to itself for 5 or 6 days, after which the distillation residues were removed. The charge of ore per furnace amounted to 49 to 58 tons; the output of mercury was 2·36 per cent., when ores containing 3·26 per cent. were treated. This output was smaller than in the case of the aludel furnace, but, on the other hand, the working expenses were also less. At present there are two Idrian furnaces in use at Almaden. Each of them is 25 feet high, and is circular in plan, with a diameter of 10 feet. As in the case of the Aludel furnace, there is here only one single brick arch with perforations.

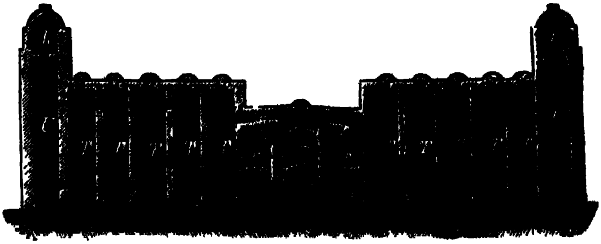


FIG. 188.

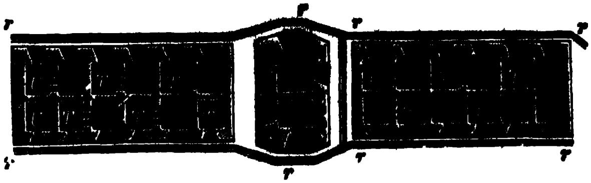


FIG. 189.

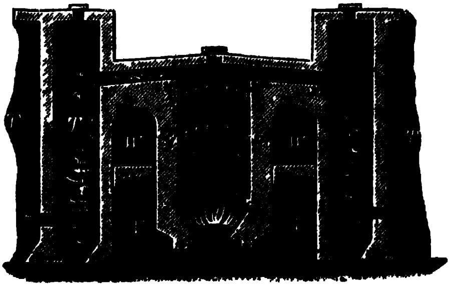


FIG. 190

There are five openings on either side in the upper part of the shaft, through which the gases and vapours escape into the condensing chambers, of which there are six on either side. As in the furnace at Idria, the last chamber is higher than the others, and acts as a stack. The other details of the chambers, the sides and floor of which are coated with Portland cement, are similar to those at Idria. The charge of these furnaces is twice that of the Bustamente furnace, viz., 27·2 to 28·5 tons of ore. The labour employed for charging the furnace is the same as for the Bustamente furnace; it occupies one day. The furnace is then fired for a day, the heat necessary for distillation being maintained during the two following days by the sulphur contained in the ore. The period of cooling, which lasts for a day, now follows, and another day is occupied in withdrawing the residues after distillation and the ashes of the fuel. Including charging and clearing, six days are therefore required for distillation. The consumption of wood for each distillation amounts to 4·2 to 4·5 tons. The soot is freed by rubbing in the condensing chambers from the greater part of the quicksilver contained in it. The residues thus obtained are agglomerated, together with ore fines, into lumps, and treated in the distillation furnace. According to experiments executed at Almaden, the losses of mercury in this furnace are higher than in the Bustamente furnace, the ratio being given as 6·2 in the former to 4·41 in the latter. These results have, however, been obtained by the old method of ore assaying in retorts with the addition of lime, and can, therefore, not be taken as reliable. On the other hand, it is perfectly clear that the working of the Idrian furnace is cheaper than that of the Bustamente furnace.[1] In Idria, where the furnaces had done better work than the Bustamente furnace, especially for ores poorer in mercury than those of Almaden, carrying 3 to 4 per cent. of mercury as against 7 to 10 at Almaden, this furnace has been thrown out of use since 1870, and has been replaced by continuous working furnaces and modern shaft furnaces.

Externally Fired Furnaces

Furnaces of this type were formerly in use upon a large scale at the Redington works, near Knoxville, and the New Almaden works, both in California, but have been replaced by modern furnaces.[2] The last furnace of this kind was in partial use in New Almaden in the year 1889, but has probably disappeared by this time. In this furnace the fireplace was built out on one side of the shaft, this side being formed by a curved perforated. wall, through which the products of combustion could enter the shaft, after which they passed through horizontal channels left in the column of ore, towards the opposite side, through which they were discharged into condensing chambers. The latter were similar to those used in the Idrian furnaces; they were, however, confined to one side of the furnace, and were present in larger numbers (from 18 to 22), terminating in a brick tower, which was again connected by means of a flue with a Guibal fan. Lump ore, as well as ore fines moulded into blocks, were treated in this furnace. Its construction is shown in Figs. 191 to 193; *o* is the

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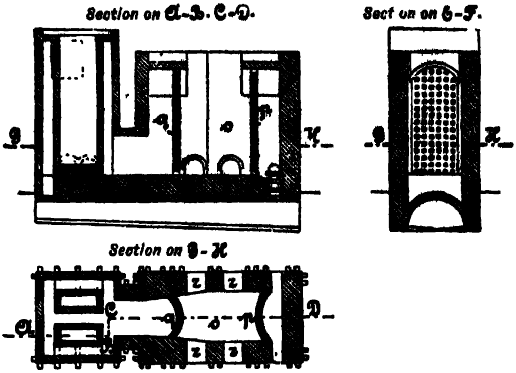
[1] Langer, *loc. cit.*

[2] Egleston, *Metallurgy of Silver, Gold, and Mercury*, vol. ii., p. 814.



FIGS. 191—193.

shaft furnace proper, *p* and *q* are brick walls perforated to their full height for the passage of the flames. They are arched in plan so as to better resist the lateral pressure of the column of ore. The fire-grate is in a chamber behind the side wall *p*, through openings in which the flames penetrate into the shaft, and, mixed with the vapours of sulphur dioxide and mercury, pass through openings in the wall *q*, into the condensing appliances. The passage of the gases through the column of ore is facilitated by means of channels left in them, corresponding to the openings in the walls of the furnace. When lump ore was treated, these channels were produced by a suitable arrangement of the lumps of ore. When both lump ore and blocks of ore fines (*adobes*), or ore fine blocks alone were being treated, the channels were constructed of these blocks. In the upper part of the ore column these channels were of a smaller section than in the lower part, in order to cause the flames to travel as nearly horizontally as possible through the furnace. The ores are let down in baskets through the furnace mouth. The residues remaining after the mercury has been distilled off are removed through the apertures *z*, *z*. The top of the ore column is sealed by a cover of old iron, straw and clay. In the first condensing chamber there are two smaller chambers for drying the ores; they are open at their upper ends, and provided with two apertures each at their lower ends for drawing out the dried ores. The furnace is 18 feet high, 9 feet broad and 12 feet long. The opening through which gases and vapours pass into the first condensing chamber is 7 feet high. The charge amounts to 90 to 100 tons, the older furnace taking charges of 50 to 70 tons only. Charging takes a day, and requires the labour of eight men. After the furnace is properly closed up, firing is continued for 4½ days. The mercury commences to condense at the end of 14 or 16 hours, and has finished after 4½ days. The furnace is then allowed to cool for 3½ days, during which time the doors of the fireplace are opened. After this time, the cover is removed and the distillation residues drawn out through the openings provided for that purpose. One man per shift is required to look after the fire. The cleaning out of the furnace takes a day and requires four men. Three charges can be worked per month. Eighteen cords of wood are required for 100 tons of ore. Upon the average, each ton of ore yielded 1,873 flasks of mercury. These furnaces have been replaced in California by continuous working furnaces, which work much more cheaply and do not require the ore fines to be moulded into bricks

The Extraction of Mercury in Shaft Furnaces Fired Continuously

To this class of furnace belong the furnaces of Exeli, of Langer, of Knox, of Hüttner and Scott, of Livermore and of Czermak. The furnaces of Exeli and Langer are suitable for the treatment of lump ores. The furnaces of Hüttner and Scott, namely, the Granzita furnace and the Tierra furnace, as also the Czermak furnace and the Livermore furnace, are suitable for the treatment of ore fines. The Knox furnace can treat both lump ores and a mixture of lump ores and ore fines, provided that the latter do not exceed a definite proportion of the whole. Both the furnaces of Exeli and Langer have given good results with lump ore. That of Knox, which was favoured for a long time in California, is now only used at one works. All the furnaces which have been mentioned as suitable for ore fines, of which the Hüttner and Scott and Livermore furnaces were invented in California, are at present in use at various works and give satisfactory results.

Furnaces for Lump Ores

Exeli Furnace[1]

This furnace was built at Idria in 1872 by Exeli. It consists of a shaft furnace, surrounded with three external fireplaces, and cased in wrought-iron to prevent loss of mercury; there is also an iron plate underneath the bottom of the furnace. The construction of the furnace is shown in Figs. 194 and 195; *S* is the furnace shaft with the three fireplaces *a*, and three openings underneath them, *b*, for the removal of the distillation residues. The residues drawn through these openings are cooled in the chamber *c*, which serves at the same time as an ashpit, wherein they may give up their heat to the air entering under the grate. In order to remove the distillation residues from the furnace, the necessary tools can be introduced through the doors *d*, into the openings *b*. The charging apparatus consists of a

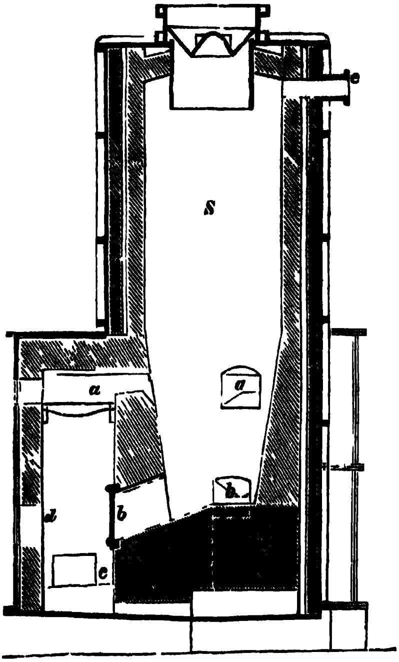


Fig 194.

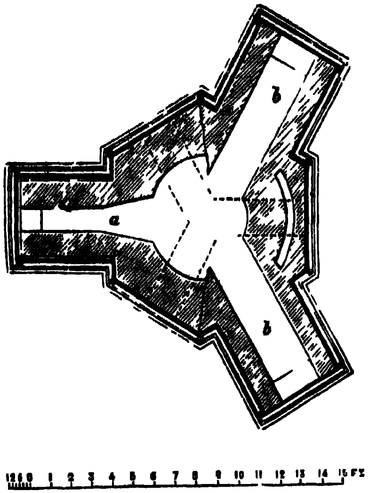


Fig 195

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[1] *Das K. K. Quecksilberbergwerk Idria in Krain*, Wien, 1881.

cup and cone with water seal. The vapours escape through the pipe *e*, into condensers. The grates are arranged for wood firing. The shaft is 13 feet high, 6 feet 3 inches in diameter in the upper part, and 4 feet 3 inches in the lower part. The grates are each 34 inches long and 12½ inches wide.

The condensing arrangement consists of cast-iron Y-shaped pipes 19 inches in diameter, followed by condensing chambers, the arrangement of which is shown in Figs. 196 and 197, in which *g* are the pipes, three rows of which lie side by side. They terminate below in short vertical branches, which are open and dip into boxes *h*, 19 inches wide, filled with water. In these the condensed mercury collects and flows off into an iron vessel, which is kept locked. The tubes are cleaned from soot by means of discs attached to rods, introduced through the upper portion of the tubes, by means of which the soot adhering to the insides of the tubes is pushed down into the boxes *h*. This furnace treated ores that would not pass through a sieve of 0·8 inch mesh, and which contained from 0·2 to 0·8 per cent. of mercury. In 24 hours 14·2 tons of ore were treated with a consumption of 102 cubic feet of cord wood. The distillation residues contained 0·002 per cent. of mercury, the total loss of metal amounting to 8·9 per cent.

By building up the fire spaces, these furnaces were afterwards converted at Idria into true shaft furnaces, in which the fuel—charcoal—was introduced together with the ores into the shaft. The Exeli condenser was open to the objection that in consequence of the inclined position of the cast-iron pipes the acid water that condensed in them ran down into the lower portion and rapidly destroyed this part. Czermak therefore employed, instead of the inclined pipes, vertical pipes lined inside with cement, the lower portions of which terminated in iron boxes, which were also protected by a layer of cement. This condenser has been replaced by the modern Czermak condenser, which effectively employs the principle of surface condensation by subdividing the mercurial vapours among several rows of narrow flat stoneware pipes. At present, therefore, as fast as the iron pipes become destroyed they are replaced at Idria by pipes of glazed stoneware.

There are two Exeli furnaces at work in New Almaden, which were built in the years 1874 and 1875. The construction of the first built furnace is shown in Figs. 198 and 199. The shaft[1] is altogether 20 feet high in the clear; the diameter in its uppermost widest part amounts to 11 feet 6 inches, narrowing down to 5 feet 6 inches;

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[1] Egleston, *loc. cit.*

whilst in the bottom portion, 8 feet in height, it narrows still

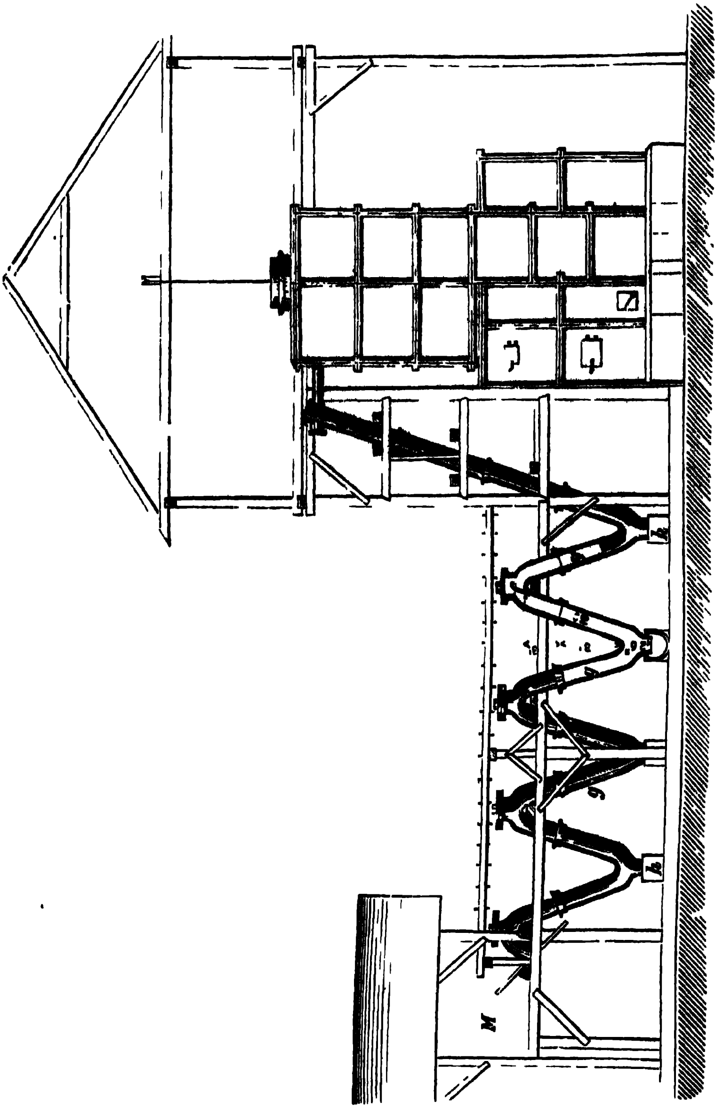

FIG. 196.

further down to 4 feet. The shell consists of wrought-iron, $\frac{1}{8}$ inch thick. It encloses first of all a shaft of common brick, and then an inner lining shaft proper of fire-brick separated from the former by a small interspace. The lower portion of the furnace, in which the fire-places and discharging doors are situated, is supported on cast-iron plates. The furnace stands upon a plate of cast-iron forming a very flat cone, so that any mercury collecting in it runs into a vessel placed under the apex of the cone. The furnace top is closed by an annular plate of cast-iron, all except the throat, which is fitted with a charging apparatus similar to that already described. When the furnace is charged, a height of 3 feet is left empty in the upper part. In this the vapours evolved during distillation collect, and escape through cast-iron pipes 1 foot in diameter, of which there were 6 in the earlier furnace, but only 3 in the later one, into a main 21 inches in diameter inclined at an angle of 10°, through which they pass into the condensing chambers. All these tubes are fitted with cleaning

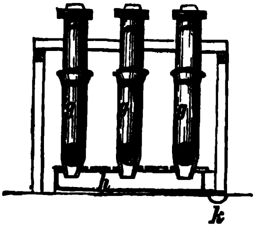

FIG 197

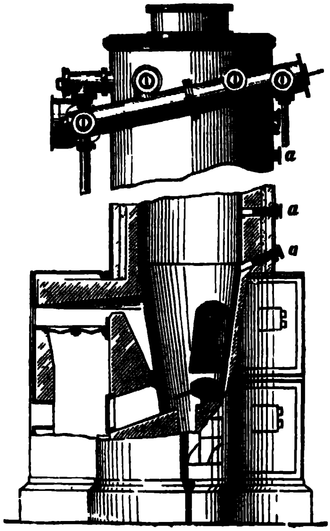

FIG. 198.

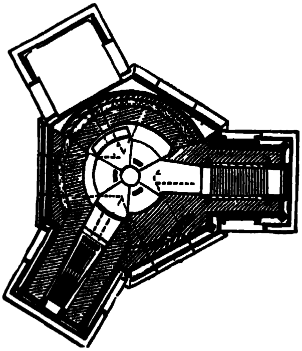

FIG 199

discs, in order to be able to remove the soot. So as to be able to observe the progress of the distillation, there are 12 peep-holes, *a*, arranged at four different heights. The condensing appliances consisted formerly of brick chambers, a Fiedler condenser, and

Fiedler-Randol glass and wood condensers. The brick chambers, of which there were 2 to each furnace, were 28 feet high, 28 feet long, and 18 feet broad. Each of these were divided into two halves by means of a partition. From these chambers the gases passed into a Fiedler condenser, the construction of which is shown in Figs. 200 and 201, and which consisted of rectangular boxes of cast-iron, 10 feet 6 inches long, and 5 feet 6 inches high and broad, the cover of which is shaped like a flat roof. It was divided into 4 divisions *Z*, by means of 3 hollow iron walls, *W*, in which water circulated, each division having an inclined bottom. The first and last of these iron walls were open above. Through the pipe *R*, the water entered the hollow walls, which communicated with each other by means of a small pipe *x*, and after flowing through these it escaped through the opening *t*.

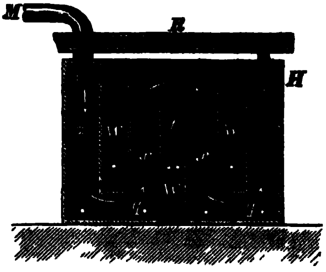

Fig. 200

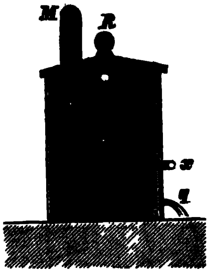

Fig. 201.

The pipe *R* also served to cool the iron roof and side walls of the boxes. The gases entered the boxes through the pipe *M*, traversed the divisions, and escaped at *H*, the products of condensation escaping through the pipe *q*. According to Egleston, this arrangement was done away with, in spite of the good results obtained from it, because it interfered with the draught of the gases and vapours, and because the iron of which it was made was strongly attacked by the condensed vapours.

The older condensers of glass and wood into which the gases passed from the Fiedler condenser are shown in Figs. 202 to 204. They consisted of rectangular wooden boxes, in the walls of which a large number of sheets of glass are inserted, but not puttied in. These boxes were divided into four divisions by means of partitions, so that the gases had to traverse them, entering at A and escaping at B. The bottom was inclined towards the two longer sides, in order to allow the condensed products to run off readily. These condensers, too, have been discontinued for the Exeli furnace, but have been retained for the furnaces which are treating ore fines.

At present the condensing plant consists of brick chambers and of cooled iron pipes. From the above-mentioned brick chambers the gases enter two systems of cooled iron pipes, and then again a series of brick chambers. From the last chamber they are conducted by a wooden box into a tower, and then through another wooden flue into a main flue common to a number of furnaces, through which they are drawn by a Guibal fan. The construction of the very effective iron pipe condensers is shown in Fig. 205.[1] From the brick chambers connected with these condensers, the gases and vapours escape through three pipes made of wrought iron 0·18 inch thick, inclined at an angle of about 20°. They are 22 inches in diameter and 19 feet long. From these they pass into three corresponding systems of tubes, which have the shape shown in the

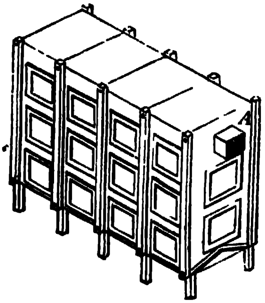

Fig. 202

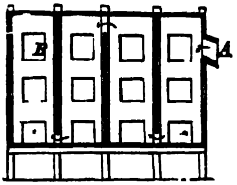

Fig. 203

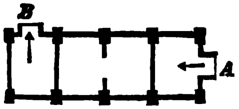

Fig. 204

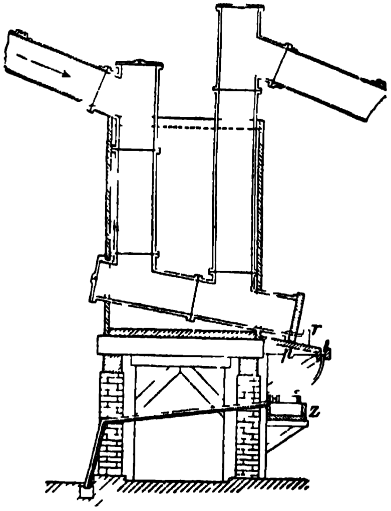

Fig. 205

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[1] Egleston, *op cit.*

figure, and which are contained in a wooden box 10 feet long, 10 feet deep, and 6 feet 9 inches broad. These pipes are made of cast-iron, and are surrounded by water, which enters the lower part of the box and escapes heated from the upper part. The pipes are 22 inches in diameter and 0·75 inch thick. The inclined pipe lying in the bottom of the box serves to collect the products of condensation. From the lower end thereof these products, namely mercury and soot, can be run off by means of a smaller pipe. They run first on to a plate *p* covered with indiarubber, upon which the soot is retained, and thence enter a vessel in which the mercury is collected, whilst the acid water runs out over its edge. The vertical, as well as the inclined, pipes terminate in blind flanges, which can be removed in order to clear out the soot. From the last vertical pipe, gas and vapour enter a brick chamber provided with movable partitions, and traverse it in the direction described above. By moving the partitions, which resemble dampers, the rate of the gas current can be regulated. The wooden flues through which the gases are conveyed to the fan are shown in Figs. 206 and 207. They are built of two layers of curved planks, between which there is a coating of asphalt. Their inner surfaces are coated with a mixture of asphalt and coal-tar, and they are coated externally with asphalt. At every 6 feet they are supported by a wooden frame. The Guibal fan, which provides the draft for five furnaces, has an iron frame, the vanes being of wood. Its diameter is 9 feet, its width 28 inches. Those parts of the fan that are made of wrought iron have to be renewed every two years. In working the furnace, it is first charged with ore containing from 5 to 8 per cent. of quicksilver, and sometimes as much as 10 per cent. The ores are mixed with 1½ per cent. of charcoal. The fuel burnt on the grates is fir wood or oak. When the furnace is in

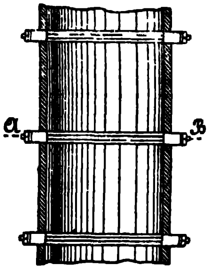

FIG. 206.

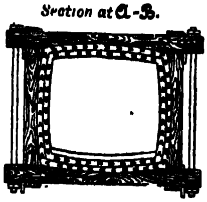

FIG. 207.

regular operation, it is charged and drawn every two hours; every charge remains about 2¼ days in the furnace. A pair of furnaces are worked by two men on the shift, 10 tons of ore (*granza*) being treated in 24 hours, the furnace being capable of putting through a larger quantity of poorer ores. The consumption of fuel amounts to 85 cubic feet of cord wood per 24 hours. According to Egleston, in the year 1888, one of the two furnaces at New Almaden was in operation for 345 days, and treated 3,185 tons of *granza* ores. The product was 7,062 flasks, each containing 76·5 lbs. of mercury, or a production of 8·48 per cent. A second furnace was only in operation 157 days, and treated 1,486 tons of ore, producing 3,050 flasks of mercury, or an output of 7·84 per cent.

The Langer Furnace

This furnace was designed in 1878 by Langer in Idria, and is a modified Exeli furnace with an iron shell. It differs from the latter chiefly in being oval in horizontal section and in not standing by itself, four furnaces, built side by side, being enclosed in one common shell. The construction of such a block of four furnaces, together with the condensing arrangement, is shown in Figs. 208 to 210; *B* are the furnaces standing upon an iron plate surrounded by a shell of iron. The shafts for a distance of 14 feet from the throat have a cross section of 7 feet 6 inches by 5 feet 9 inches, and contract from this to the bottom of the furnace, a height of 9 feet, to a cross section of 5 feet 9 inches by 3 feet 8 inches. On either side of the furnace there are two step grates, making altogether four fireplaces *c*. Beneath each of these are the four openings *a*, *b*, through which the distillation residues can be drawn out. Charging is effected by lifting the cone *D* by means of the rod *d*, in the casing *C*. The upper end of the latter is closed by means of a cover *n*, provided with a water seal, the cover being made of wood and balanced by means of the counterpoise *p*. The gases and vapours escape through the upper part of the furnace into cast-iron tubes *E*, 18½ inches in diameter in the clear, there being three of these tubes to each furnace, which are provided on either side with two oval openings, through which the gases and vapours enter the tubes. These tubes communicate with the condensing tubes proper, which are also made of cast-iron. There are three rows of these tubes for each furnace, surrounded by the cooling box *K*, in which a constant current of cold water circulates to promote condensation in the same way as has been explained on page 285. The cold water enters through the tube *h*, at the bottom of the box, the heated water running out at the upper part through the tube *i* and the gutter *k*, and thence into the sump *m*. The products of condensation collect in the box *G*, from which the mercury, with a portion of

Section on *A B*

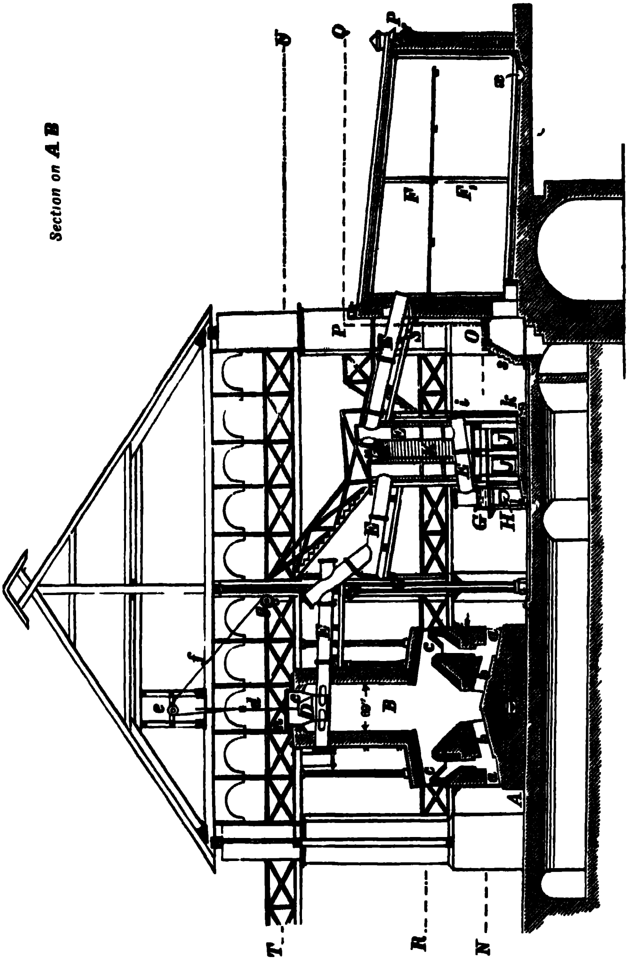

Fig. 208

soot, is run off into the reservoir *H*. The acid waters are run out of the soot collector *G*, alternately into two soot tanks *I*, and after settlement are run off through the gutter *k* into the sump *m*. The gases and uncondensed vapours pass into the condensing chambers

P, which are built of brickwork pointed with cement. The walls are covered first with asphalte, then with a layer of cement, and finally with smoothly planed wood. The bottom of the chamber consists of a layer of concrete 3 inches thick, upon which there is a thick asphalte pavement. The cover of the chamber consists of the dished-out cast-iron plates *O*, which are bolted together, the joints being made with rubber. This cover is cooled by means of a stream of water conducted over it. The chamber is divided by wooden par-

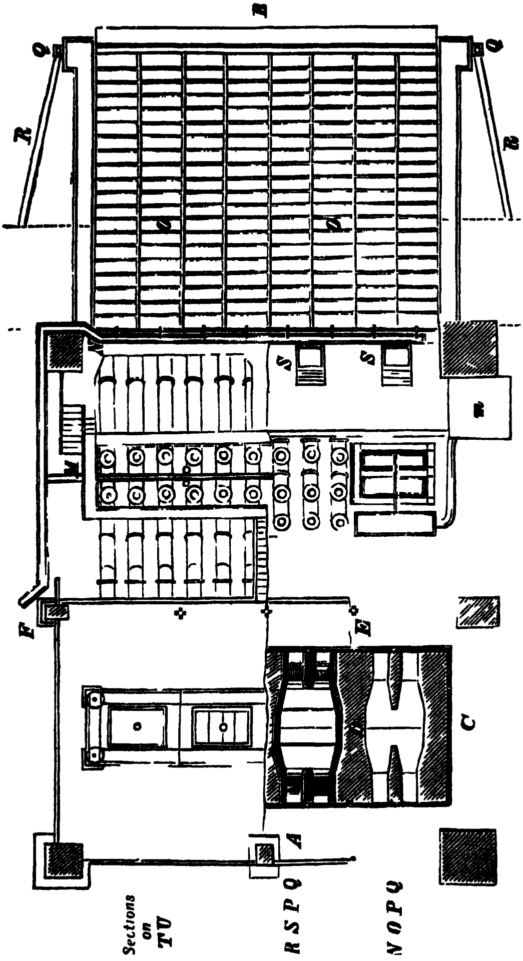

FIG 209

titions into four divisions corresponding to the four furnaces. Each of these divisions is divided by a horizontal partition into an upper chamber F and a lower one F'; from these chambers the gases pass through the flues S into a subterranean system of chambers, thence into a series of central chambers common to the whole furnace, and finally pass to the stack or fan. One of these furnaces used to put through in 24 hours 15·9 tons of lump ore containing 0·2 to 0·8 per cent. of mercury, 24 cubic feet of wood being consumed to each 100 tons of ore. In 1893, the loss of mercury was 9·12 per cent. according to Exeli. The fireplaces of these Langer furnaces have at present been bricked up, and they are used as shaft furnaces proper, into which the ores are charged together with charcoal. The condensing arrangement has been replaced by Czermak condensers with stoneware pipes.

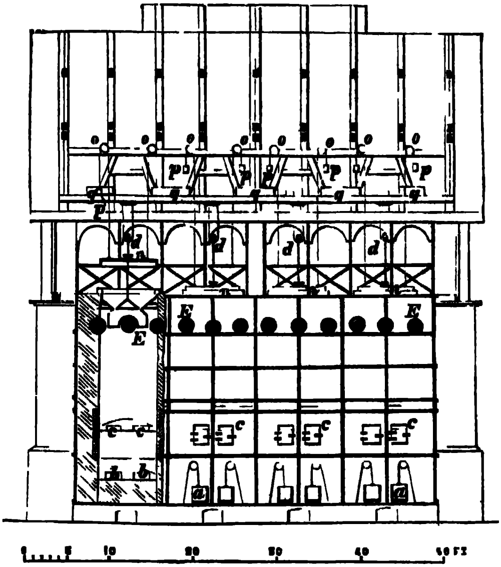

FIG. 210.

The Knox Furnace

This furnace was erected in the years 1874 to 1875 at the Redington Mine, and was also introduced at a number of other Californian works. It was intended to treat simultaneously lump ore and ore fines. Although it gave good results, both for lumps and for mixtures of lump and fine, provided the latter did not exceed a definite proportion, and showed itself especially far superior to the modified Idrian furnace, it has not come into general use, as was at first expected, in consequence of the construction of furnaces specially for the treatment of ore fines, and on account of the existence of other good furnaces suitable for the treatment of lump ores. At present, since the works at which it was first introduced are no longer in operation, it is only being used at the Redington Mine. Its special advantage is said to be that it will treat satisfactorily ores containing only 1½ per cent. of mercury. Its construction is shown in Figs. 211 and 212. It consists of a brick shaft with

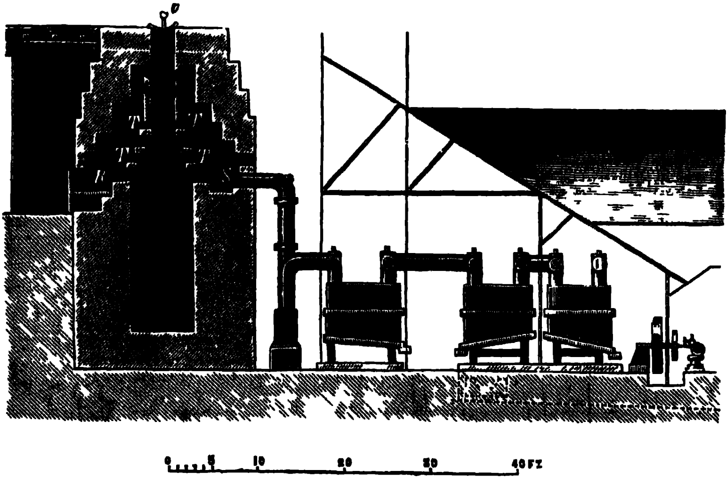

FIG. 211

walls widening upwards stepwise, and with a lateral fireplace in the middle of its height. The height of the furnace, of which two, or in case of need four, are best built side by side, amounts to 39 feet. The shaft is rectangular in horizontal section. As shown in the figures, the furnace widens from the throat to the fireplace, the latter lying 20 feet below the former. The shaft proper is, as is shown, 7 feet square. In order, however, to heat the ores thoroughly, the side containing the fireplace has been brought nearer the opposite side, to within 2 feet in the newer furnaces, according to Egleston.[1] At the level of the fireplace the cross-section of the shaft therefore presents in these furnaces a rectangle of 7 feet by 2 feet. . At the opening for the removal of the residues, the cross-section decreases again down to 2 feet by 2 feet. The arches *T* form two chambers, *R* and *S*, the former of which contains the fireplace, whilst the escape pipe for the gases and vapours lies in the second. The five arches *T*, of which the two top ones are smaller than the rest, are spaced some distance apart, leaving openings, through which the flames enter the shaft at one side, and escape at the opposite side into the chamber *S*. By means of this arrangement, the flames are forced to traverse the column in the shaft in a horizontal direction, and, together with the products of oxidation of the sulphur and the mercurial vapours, are drawn by means of a fan into the condensers. The three lowermost arches are stepped backwards, so that the shaft proper widens out at this point. Owing to this widening the column of ore is rendered loosest opposite the fireplace in order to promote a better circulation of the flame through the ore, and also to avoid any ore dropping through the slots into the above-mentioned chambers.

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[1] *Op. cit.*, p. 842.

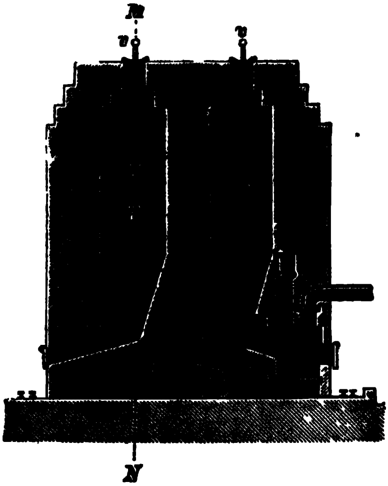
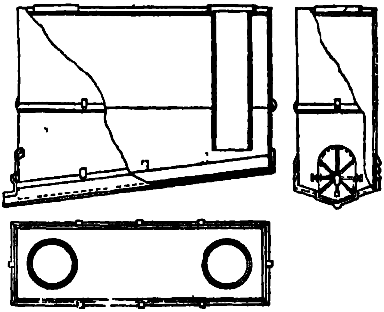


Fig. 212

The fire heats the ore to such a temperature that it will continue to burn by itself in the lower part of the shaft; *z* is the opening through which the residues of distillation are drawn out. The throat is closed by a cover *v* in the shape of a segment of a sphere, which is pushed to one side by means of a projection on the ore waggons. The bottom of the chamber *S* is covered with stout plates of iron, which are to prevent the penetration of the mercury into the brickwork. From this chamber the gases and vapours pass by means of a cast-iron pipe, 1 foot 6 inches in diameter, into Knox-Osborne condensers. These consist of a series of 16 to 19 boxes of cast-iron and wood, rectangular in horizontal section and with an inclined floor. which are united by means of cast-iron elbow pipes. The construction is shown in Figs. 213 to 215; the boxes are 8 feet long, 2 feet



FIGS. 213—215.

6 inches broad, 5 feet high at one end and 6 feet at the other. They are cooled by allowing water to trickle first over the cover and then over the sides. The last eight boxes are made of wood. As the bottoms of the iron boxes are constantly covered by a layer of fluid, they are not more strongly attacked than the sides; in consequence of this observation, the thickness of the bottom plates, which was first very great, has been diminished. Attached to the last condensers is a Roots blower, one to each furnace, which draws the gases through a wooden flue into a wooden tower 15 feet high and 4 feet in section. This tower is filled with stones, over which water trickles, so as to condense the last particles of mercury. The uncondensed gases escape from the tower through a long flue to the summit of a hill, where they are allowed to escape into the open air. The products condensed in the boxes flow through an opening at the lower end of the inclined bottom plates into gutters, and thence into a pan, from which the mercury is ladled out, whilst the acid waters are run into settling tanks, in which any metallic particles carried by them are deposited. On account of the high temperature of the gases and vapours as they enter the condenser, the greater part of the mercury is deposited only in the middle boxes of the series, whilst relatively large quantities of acid waters are condensed in the last boxes. The ores are charged and the residues drawn at intervals of an hour. In normal working 1 ton is charged at a time, so that the furnace puts through 24 tons in 24 hours, the ore taking three days to pass through the furnace. At the Redington Mine the charge consisted, according to Egleston, of ½ to ¾ of coarse ores and ½ to ¼ of fines, the average quicksilver contents being 1½ per cent. When the larger quantities of fines were charged, or when the ores were damp, the furnace was unable to treat more than 12 tons per 24 hours. At the Redington Mine, when good wood was employed, its consumption amounted to 1 to 1½ cords per double furnace, according as the charge contained more or less fine ore. A single furnace treating 24 tons in 24 hours required six men during that time, a double furnace treating 48 tons eight men, and a block of four furnaces treating 100 tons 10 men. The

removal of soot from the condensers and tubes took place once a week; it only takes a few minutes for each of the boxes. On account of the powerful action of the blower, no gas or vapours can escape from the boxes during this process, so that the health of the men engaged in the operation is not impaired. There are no data as to the losses of mercury. As already stated, these Knox furnaces are now no longer built.

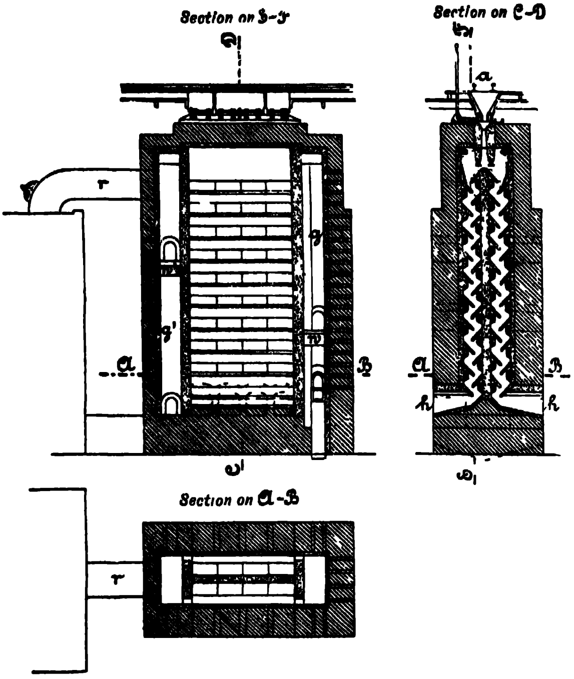
FURNACES FOR ORE FINES

Hüttner and Scott Furnaces

Hüttner and Scott have designed furnaces for the treatment of coarse-grained ores, known as *granzita*, of 3·2 to 1·2 inches cube, as also for the treatment of fine ore, known as *tierras*, less than 1·2 inches cube. These furnaces, which were first introduced at New Almaden in the year 1875, are shaft furnaces externally fired, in which the free fall of the ore through the shaft is prevented by means of inclined shelves, sloping at an angle of 45° in alternately opposite directions, upon which the fine ore (the angle of repose of which amounts to 33°) slips down, as in the case of the Hasenclever and Helbig furnace (Vol. I., p. 56). In these furnaces, however, the residues are not removed continuously as in the last-named furnace, but are drawn out from it at short intervals. These furnaces have given excellent results, and are largely used at New Almaden.

The Granzita Furnace

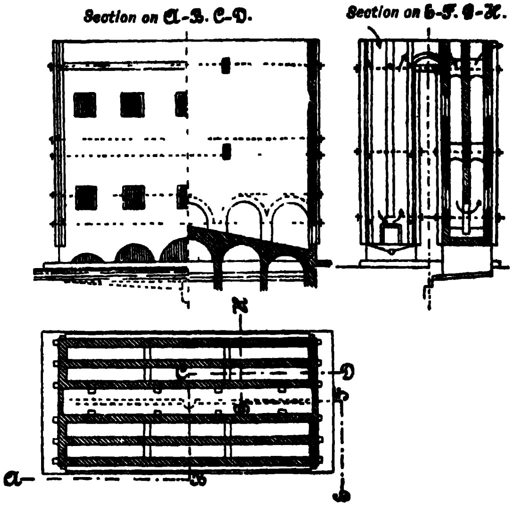
This furnace is distinguised from the *tierras* furnace principally by the interval between each pair of alternately inclined shelves being greater than in the case of the latter, amounting to 7 inches, and by the removal of the residues being performed without the aid of shaking appliances, as in the case of the tierras furnace. The older furnaces were built with two shafts, whilst the most recently built consist of four shafts in one block, with a common fireplace. The general construction of the two-shaft furnaces is shown in Figs. 216 to 218. Each shaft is fitted with shelves inclined alternately at angles of 45°. As soon as the residues of distillation are drawn out through the apertures provided for that purpose, the ore lying above them slips down. The topmost shelves thus become free, and are then recharged with ore, the charging being performed by means of the hopper *a*. The flame and air pass in the opposite direction to the ore, and heat the shelves both below and above. The gases are compelled to travel this particular path by means of the partitions w and w', made of fire-brick; from the grate lying beneath the partition w they enter the space g', and then traverse the lowest third of the furnace longitudinally. Being prevented by w' from rising upwards in the chamber g', they are compelled to traverse the second third of the furnace into the chamber g, and from it have to traverse the remaining third, entering the pipe r, which leads them into the condensing appliances. Each shaft is 27 feet 6 inches high, 2 feet 6 inches broad, and 11 feet 6 inches long. There are ten inclined tiles on either side of the shaft. The vertical chambers in which the above-named partitions are arranged are 2 feet 6 inches wide. The ore, which is charged by means of the hopper a, is passed through a sieve of 3·75 by 2·5 inches mesh. The hopper is closed at its lower end by means of a conical valve. The distillation residues are drawn out at intervals of 40 minutes in quantities of ½ ton each time for the two shafts, a corresponding quantity of ore being charged in the furnace at corresponding intervals. In 24 hours the two shafts



FIGS 216—218

together put through 18 tons of ore with a consumption of ¾ cord of wood, three men being engaged on the furnace per shift. In 1888, this furnace was in operation for 128 days at New Almaden, and put through 2,375 tons of ore, producing 1,239 flasks of mercury, equal to an output of 1·995 per cent.

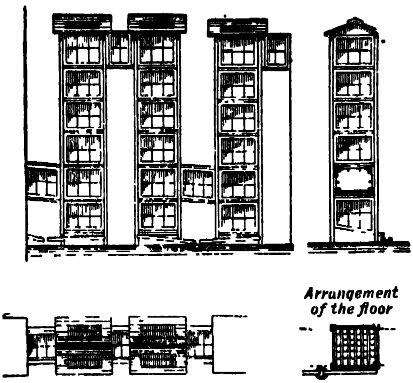
The condensing appliances are chambers built partly of brickwork, partly of glass and wood. The condensers of glass and wood form the last chambers into which the gaseous current enters after it has been cooled. The construction of the brick condensers is shown in Figs. 219 to 221. They consist of chambers



FIGS. 219—221.

27 feet high and 6 feet broad, divided by a brick partition into two divisions. The chambers are connected by means of brick flues 4 feet square; for the convenience of cleaning them out, there are two rows of openings 2 feet square in the side walls. These are closed by iron plates in the hotter chambers, and by sliding windows in the cooler ones. The floor is coated with cement, on top of which there is a layer of asphalt in the cooler chambers. The floor is inclined towards the centre, as also towards one side. The walls of the cooler chambers are coated with a mixture of asphalt and coal-tar. The path of the gases and vapours through the chambers is indicated by arrows; they enter the upper part of the condenser, traverse the first division, enter the second division from below,

traverse it and escape at its upper end into a second condenser, which they traverse in the same direction, pass through the following condensers, and finally reach the fan. The mercury is deposited upon the inclined floor of the chambers, and flows through a gutter in them into an external gutter made of brickwork and lined with asphalt, from which it runs into the collecting pans. Quite recently the walls of these brick condensers have been provided with so-called water backs, consisting of cast-iron boxes 43 inches long, 16 inches wide, and 14 inches deep, in which water circulates. They are provided with an external flange 8 inches broad, to which the cover lined with wood is bolted. There is a partition in them which forces the cold water, entering at the bottom by means of four pipes, to circulate. These water backs are applied to the first two chambers; they have given good results, and compel by far the greater portion of the mercury to condense in the first brick chamber, whilst it used formerly to be deposited in the fourth to the seventh chambers. Their life is up to four years. Chambers provided with these water backs are considered at Almaden to be the best of all condensing appliances, and have to a great extent replaced glass and wooden condensers.



FIGS. 222—224.

The arrangement of the most modern type of condenser, made of glass and wood, of which there are 12 to 15 following the brick condensers, is shown in Figs. 222 to 224. They are connected with each other alternately above and below, and consist of towers 25 feet high and 4 feet square. They are built of glass plates let into wooden frames and contain no iron whatever. The floor consists of plates of glass lapping one over the other like the slates of a roof, and it inclines towards the side, at which there is a gutter for the removal of the mercury. This gutter terminates in an earthenware pot for the collection of the mercury. The roof and the flues uniting the towers are also built of glass. The gases and vapours are forced to alternately rise and descend in these condensers. Very little mercury, but a great deal of acid water, is deposited in these condensers, the temperature of which varies from 55° to 80° Fahr. In order that these condensers may remain tight, they must be kept in continuous action, otherwise the wood shrinks for want of moisture. From the glass chambers the gases pass through a wooden flue of the construction described on page 285 into a tower of brickwork, from which they are drawn off by a Guibal fan and forced into a stack

The arrangement of the most modern Granzita furnace[1] with four shafts is shown in Figs. 225 to 227, which represent a double furnace of the above kind. Fig. 225 shows an elevation and a vertical section on *Z Z*: Fig. 226 a vertical section on *O P Q R*; Fig. 227 a horizontal section on *V W X Y*. The entire furnace is 36 feet high, 25 feet 6 inches long and 17 feet 6 inches broad. The floor of the furnace is rendered impervious to quicksilver by means of cast-iron plates *a*. There are four shafts in the furnace, with one fireplace common to all. The dimensions of each shaft are 27 feet high, 11 feet 6 inches wide and 26 inches deep. The tiles upon which the ore slips down are inclined at an angle of 45°, the distance between two tiles inclined in opposite directions amounting to 8 inches. *J*, *J* is the grate burning wood as fuel, and fired from two opposite sides. The air required for combustion is supplied by means of the pipe *g*, which traverses a portion of the condensing chambers, and is thereby heated; it enters by means of a number of small flues under the grate. The flame passes in the same direction as it does in the Granzita furnace with two shafts. At the two narrow sides of the shaft there are chambers, III and IV, with their partitions *m* and *n*. The flame passes from the grate *J*, *J* in the lower part of chamber III up to the partition *m* in this chamber, and then passes through the openings *X* into the lower third of the four shafts, which it traverses lengthwise, escaping through the openings *XI* into the chamber *IV*. In this chamber there is a partition, *n*, at two-thirds of its height, which forces the gases and vapours to traverse the second third of the four shafts lengthwise, entering the chamber III through the openings *XI*. From the latter chamber they enter the last third of the four shafts, traverse it, and pass into the upper portion of the chamber *IV*, from which they are conveyed by the cast-iron pipe *Q* into the condensers. The openings *XI* have an inclined floor, so that any soot collected in them can slide down, the object being to prevent the openings becoming stopped up either partially or entirely. In order to keep all the openings clear, and to prevent the ore settling upon and between the inclined tiles, as is apt to happen in the case of wet ores, gas pipes 3 inches in diameter are built into the wall of the furnace opposite each partition. These pipes are kept closed during the operation by means of clay plugs, and through them iron bars *L* can be introduced, by means of which any flue-dust can be removed through the doors *M*. Any ore that has

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[1] Egleston, *op. cit.* p. 877; *Eng. Min. Journ.*, 1885, p. 174.

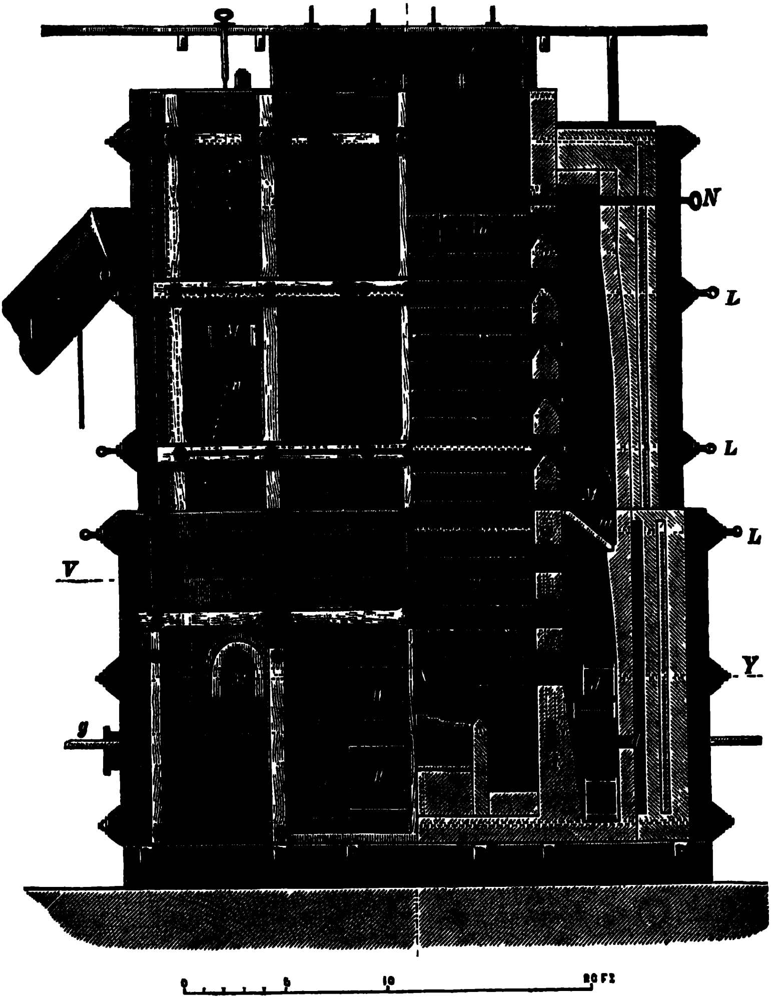

FIG. 225.

fritted on to the topmost tiles can be removed by means of the iron rabbles *O*, which are attached to the sliding bar *N*; *t* are the

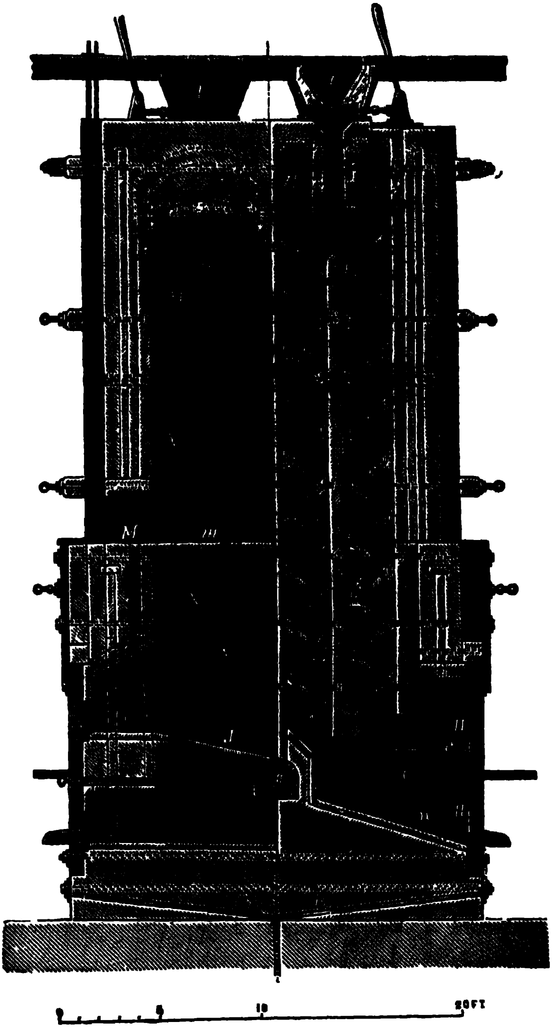

FIG. 226.

charging hoppers, the lower portion of which is closed by means of slides controlled by a lever; *u* are openings that can be closed by means of doors, through which the residues of distillation can be removed from the furnace. There are 4 such openings on either of the longer sides of the furnace. The distillation residues from the inner shafts fall direct upon the inclined floor of the furnace which is covered with cast-iron plates. The distillation residues from the outer shafts fall upon the plate *c*, and can only drop on to the bottom of the furnace after the slide *e* is drawn back. These residues are drawn out from each side of the furnace at intervals of forty minutes, one-eighth ton being removed from each of the 8 openings, so that 2 tons altogether are removed from the furnace every 80 minutes, a corresponding quantity of fresh ore being charged at equal intervals. The ore remains for 30 hours in the furnace, the quantity of ore put through in 24 hours amounting to 36 tons, during which time the furnace consumes from 1½ to 1¾ cords of oak wood. Five men work a furnace in a shift when it

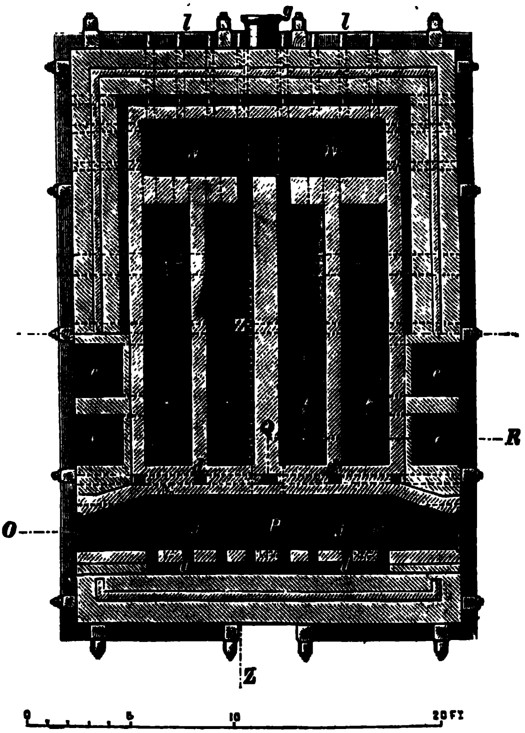

FIG. 227.

alone is in operation. If the above described 2-shaft furnace works at the same time, 3 men are sufficient. The percentage of mercury contained in the ores treated in this furnace is often as low as ¾ to 1 per cent. In the year 1888, this furnace was in operation 236 days and treated 8,420 tons of ore, from which 3,073 flasks of quicksilver were obtained, equal to 1·395 per cent. of mercury. This furnace is to be preferred to the 2-shaft furnace, as may be inferred from the fact that the costs of treating a ton of ore amounted to $0·64, whilst in the 2-shaft furnace they amounted to $1. In the former furnace wages amounted to $0·28, in the latter furnace to $0·46.[1]

The condensing arrangements consist of brick chambers and chambers of glass and wood as in the 2-shaft furnaces. The two first brick chambers and the fourth chamber are fitted with cast-iron water-backs let into the sides as already described. The third chamber contains drying kilns for the fine ore, which promotes the cooling of the gases and vapours. There are 2 water-backs in each of the brick chambers, there being 10 of these altogether, followed by 15 condensers of glass and wood. From the latter the gases escape into a brick tower and are finally conveyed by a flue to the Guibal fan, which forces them into a stack.

The Tierras Furnaces

These furnaces are similar in construction to the Granzita furnaces, except that the interspaces between the inclined tiles are smaller, amounting to from 3 to 5 inches, whilst the distillation residues are withdrawn by means of so-called shaking tables of cast-iron. Some furnace blocks have been built with 2 rows of 2 and others with 2 rows of 3 shafts; the construction of the blocks containing 3 shafts in the row is shown in Figs. 228 and 229. The fireplaces and the arrangements for deflecting the flames are the same as in the Granzita furnace. The whole furnace is jacketed with iron. The interspaces between the tiles of the outer shafts are 5 inches wide, those of the inner shaft 3 inches. It was thought that ores of rather coarse grain (Granzita) could be worked in the outer shaft. Nevertheless it was found that the heat which was quite sufficient for tierras, was not high enough for the coarser ore, so that the furnace is only treating tierras at present. Each shaft is 31 feet high, 23 inches broad and 9 feet long. The grate is 5 feet above the discharging openings, these being protected by cast-iron plates; their width is 3 or 5 inches, and they extend over the total

[1] Egleston, *op. cit.*, pp. 873, 879.

length of the furnace. Below them are the cast-iron shaking tables, which are carried upon wheels running upon rails. When these tables are immediately below the discharging openings they support the distillation residues that drop upon them until they reach their natural angle of repose. As soon, however, as the tables are pushed backwards and forwards by means of levers, the residues slide into a waggon running beneath them. The residues are thus removed every 10 to 15 minutes, a ton being withdrawn from every pair of shafts in 2 hours, and an equal quantity of fresh ore charged.

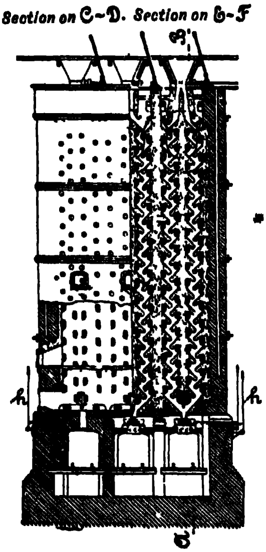

FIG. 228.

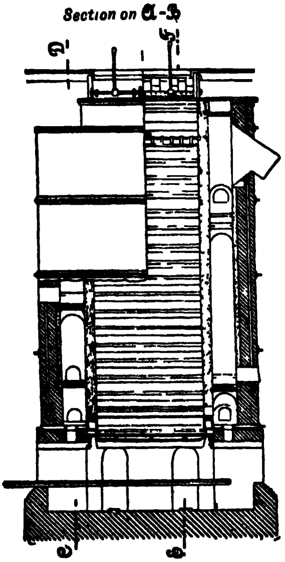

FIG 229.

The total quantity of ore, which all the 6 shafts of the furnace are capable of putting through in 24 hours, amounts to 36 tons, 2½ cords of wood being used during that time. The ore remains about 34 hours in the furnace. There are three men on the shift. In the year 1888 this furnace was in operation for 255 days, treated 9,111 tons of tierras and produced 3,078 flasks of mercury, equal to an output of 1·29 per cent. The cost of treatment of a ton of ore amounted to $0·72.

The double furnace with 2 pairs of shafts put through 24 tons in 24 hours with 2 men on the shift. At first the cost of treatment per ton of ore amounted to $1·73, but later was reduced to only one-half of that amount. In the year 1888 this furnace worked for 200 days, treated 4,737 tons of tierras, and produced 1,686 flasks of mercury, equal to 1·36 per cent. Nothing is said with regard to the loss of mercury.

The mercury is condensed in brick chambers, some of which are fitted with water-backs. A portion of the hot gases and vapours surrounds a drying kiln for the damp smalls and is afterwards introduced into condensing chambers. These shelf drying kilns are fitted with inclined tiles like the Tierras and Granzita furnaces. They are fully described in Egleston's work, Vol. II., page 871. Both the Granzita and Tierras furnaces described give exceedingly good results, but nothing is known as to the loss of quicksilver in operating them.

The Livermore Furnace

This furnace was introduced by C. E. Livermore at the Redington Mine, Knoxville, California. It consists of a row of narrow channels lying side by side and inclined at 50°, in which the flame ascends, whilst the ore, the descent of which is repeatedly interrupted, slides down upon the floor of the channels, dropping at last into a cooling chamber. The principle upon which the construction of the furnace depends is that of the older zinc blende calcining furnaces of Hasenclever (see page 59). The construction of the furnace is shown in Fig. 230. *S* is one of the inclined channels, the length of which varies from 30 to 35 feet according to the nature of the ore; the width is 6¾ inches, and the height from the floor to the crown of the arch 12 inches. There are 11 to 20 of these channels side by side, and they are heated by means of the grate *R* which is common to 10 or 11 of them. In the channels there are numerous projections, *v*, built of fire-brick and made roof-shaped, running across the channels, their object being to prevent the ore from sliding down too quickly. These project 5½ inches above the floor, and are 12 inches apart from each other. In the arch of the channels there are also projections built of fire-brick 4 inches in depth, placed half-way between each pair of projections from the floor, their object being to prevent the flame from following straight along the arch, and to force it down upon the ores. The fire grates *R* are 24 inches high and 26 inches broad; their length depends upon the number of channels lying side by side. Several fireplaces are required for a large number, whilst one fireplace fired from both sides suffices for 10 to 11 channels. The firebridge is 20 inches above the grate, and its top edge is 18 inches below the crown of the arch of the channel.

The ore is charged through the hopper *w*, the lower end of which is 2 inches square. If it should become stopped up, it is cleared by means of iron bars introduced into the hopper. The distillation residues pass at the lower end of the channels through flues *u* into the cooling chamber *B*, in which they are allowed to cool for awhile, and are then removed in waggons; the cooling chamber is connected with a condenser *T* by means of flues which collect any vapours escaping from the hot residues. *P* is an auxiliary fireplace for heating the floor of the channels. It has, however, been found unnecessary, and it has been omitted in the more modern furnaces. The roofs of all the channels are covered with ashes in order to keep the heat together. There are sight-holes in the lower portion of the shafts in order to enable the process to be watched.

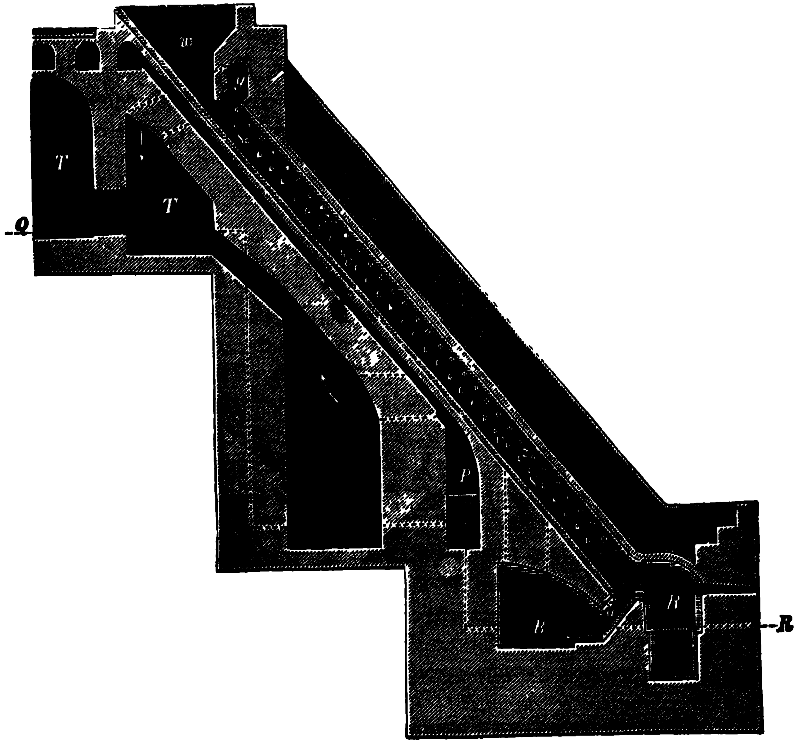

FIG. 230.

The vapours and gases escape from the flues *y* into the condenser, which consists of 5 brick chambers, *T*, 10 feet 9 inches high, 15 feet long and 4 feet wide, followed by 10 Knox-Osborne condensers, which have been described on page 291, and finally by 5 wooden chambers with inclined floors, 8 feet in height, 20 feet in width 6 feet high at one side and 5 feet at the other. Finally the gases pass through a long system of flues into a stack.

In a furnace composed of 10 to 12 flues, 1¾ tons of ore are treated per flue in 24 hours, so that the whole furnace treats from 17½ to 21 tons; in the larger furnaces each flue will put through 1 ton in 24 hours. The consumption of fuel in a furnace with 10 to 12 flues is from 1½ to 2 cords of wood per 24 hours. Such a furnace is worked by 6 men in two 12-hour shifts.

At the Sunderland Mine there is a Livermore furnace with 12 flues, which treats 15 to 16 tons of ore in 24 hours. The condensing appliances there consist of wrought-iron tubes 18 inches in diameter. At the Redington Mine there are furnaces with 16 and 20 flues respectively, the latter putting through 30 tons of ore in 24 hours. The Livermore furnaces have given very satisfactory results, although nothing is known about the losses of mercury in this furnace. According to Egleston,[1] the losses of mercury in California are said to amount to 15 to 20 per cent. in the best furnaces. At New Almaden the losses were said to amount to 7·29 per cent., according to some experiments which were extended over but a short time. Egleston says that in California the expense of further decreasing the loss of mercury is greater than the additional value thereby obtained.

The Czermak Furnace (*Schüttofen*)

This furnace was introduced in 1886 by Czermak, in Idria, and was modified by Novak, the improved form having given very satisfactory results. It is far superior to the long-bedded calciners, in which a portion of the fine ore is also calcined at Idria. The furnace consists of a shaft furnace with an iron shell; inside the shaft there are several rows of ridges made of fire-brick, the topmost row alone being of cast-iron, upon which the ore slides down. This arrangement somewhat resembles the Gerstenhöfe calciner, except that in the latter the ore bearers are ridge-shaped below and flat above. The air required both for the complete combustion of the fuel, as also that required for oxidation, is heated. Four furnaces are combined to form a block. In the most modern furnaces there are 5 rows of 6 ridges each, of which the 4 lowermost rows are built of fire-brick, whilst the upper one consists of cast-iron. The construction of a furnace with only 4 rows of ridges is shown in Figs. 231 and 232. In the former, *u*, *u* are the ridges lying one beneath the other. They are so disposed that the ore charged upon the topmost row of ridges slides gradually down their inclined faces, and reaches the bottom

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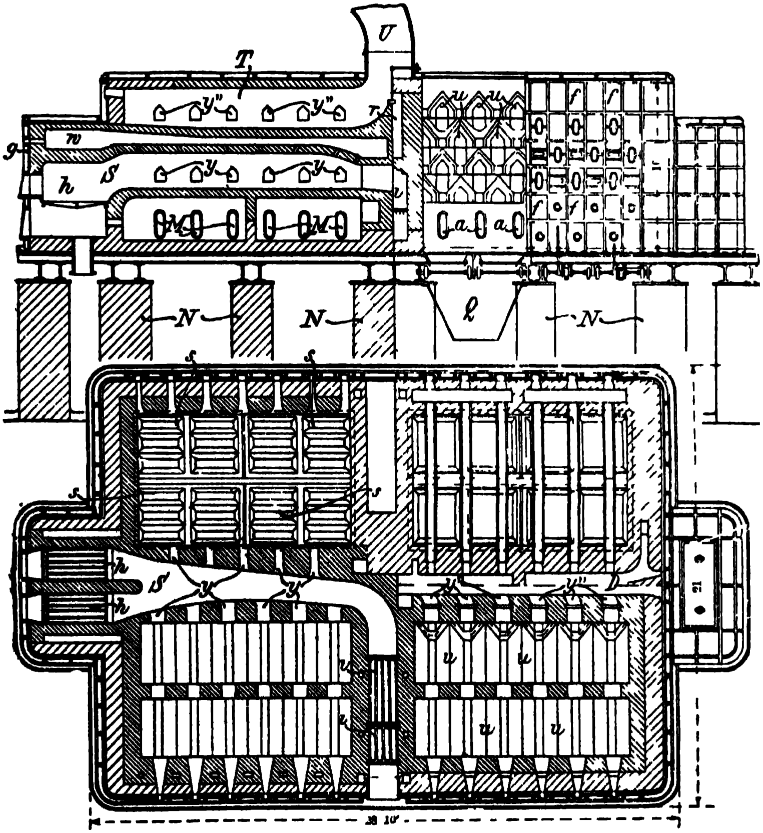
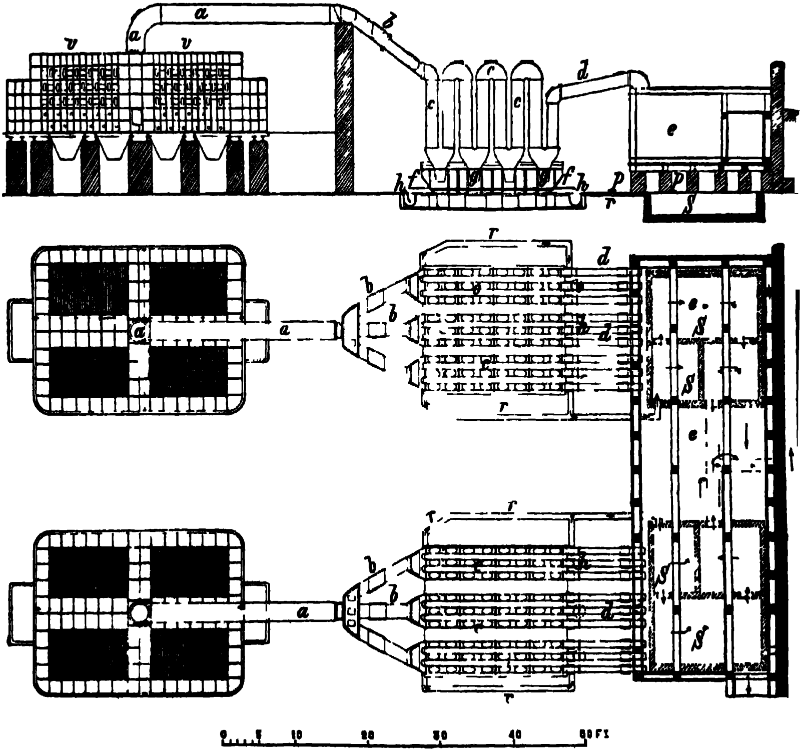
[1] *Op. cit.*, p. 899.



FIGS. 231 AND 232.

of the furnace free from mercury. The firing is done by means of the grates *h*, *i*, of which *h* is the main grate, *i* an auxiliary one. The flames from both fireplaces unite in the flue *S*. The air required for the combustion of the fuel, as also for the oxidation of the sulphide of mercury, is heated both in the elliptical cast-iron pipes *a*, as also in the lateral air chambers *r*. From the pipes *a* the air passes into the air chamber M, and from the latter, by means of vertical openings in its roof, into the flue S, in which the gases evolved from the fuel are completely burnt. Above the shaft S there is a second air chamber w, into which air passes both from the chamber r and through the openings g. The air contained in this chamber enters the flue S through openings in the floor of the chamber: from that flue the products of combustion with the excess of air enter the furnace through the openings y, y. Below these openings there is a tier of smaller openings not shown in the figures, through which the flames pass beneath the lowermost row of ridges. The flames and air ascend in the shaft in the interspaces between the ridges and finally escape laterally through the openings g'', which correspond to the spaces beneath the topmost row of ridges, whence they pass into the flue T, which carries all the gases and vapours evolved from the furnace through the pipe T' to the condenser. The fine ore falling down in the furnace finally drops through the slots s, s in the floor of the furnace, into the sheet iron hopper Q, and thence into the spaces between the columns N. The whole furnace stands upon a dish made of riveted sheet-iron which is supported by means of cement pillars protected with cast-iron plates. These pillars are let into the floor which is carefully cemented, and in which there are cast-iron tanks, so that any escape of mercury is at once perceived. The residues are drawn out and fresh ore is charged at intervals of two hours.

The condensing appliances consist of vertical pipes elliptical in cross section, made of stoneware, and cooled by means of water, followed by dust chambers. The individual portions of the system of tubes are connected by means of cement, the whole system being supported by a wooden frame. The bottom-most ends of the pipes dip for 2 inches into boxes made of iron and lined inside with cement, and filled with water, in which the condensed mercury and soot collect. A furnace with 4 shafts is connected to 8 rows of tubes with 8 vertical tubes in each. These rows of tubes open into dust chambers built of 2 inch boards, which are made tight by grooves and feathers, and cemented with a cement made of quicklime and linseed oil. The dust chambers are supported upon brick pillars, their floor being protected by a layer of Portland cement 2·4 to 3·2 inches deep. The space below the chambers forms a sump for the escaping condensed water and for the wash water. The ground about the condensers is concreted, channels being made in the concrete, through which the condensed water and wash water can run into the sumps, which are also built of concrete. The construction of the condensers for a block consisting of 4 furnaces, the mode of connecting it with the furnace and with the dust chambers, as also the construction of the latter, is shown in Figs. 233 and 234. The gases and vapours from the 4 separate furnaces *V* collect in the gas-main *a*, and pass from it into 3 branch pipes *b*, through which they enter the condensers *c*. Below the latter are the



FIGS. 233 AND 234.

boxes *f*, filled with water into which the ends *g* of the Y-shaped pipes dip. Through these boxes mercury flows off into the cast-iron pans *h*; the gases and vapours pass from the condensers *d* into the dust chambers *e*, which are provided with partition walls, and from the latter into the so-called central chambers. Below the dust chambers there are brick sumps *S*, into which the condensed water and wash water flow through the gutters *r*. *P* are the brick pillars which carry the dust chambers. Fig. 233 shows the combination of 2 blocks of furnaces with the condensers and the dust chambers. The cleaning out of the condensers, that is to say, the removal of the mercury from the stoneware pipes into the iron boxes, is undertaken every fifth day, when rich ores are treated, but only every 14 days when poor small ores of the first and second quality and poor coarse ores are treated. According to the results obtained in the year 1892,[1] furnace No. 1 at Idria treated in 24 hours 22·4 tons of poor and rich small ores, with a consumption of 130 cubic feet of wood, and a cost in wages of 17*s.* 9*d.* for every 10 tons of ore. The production of soot amounted to 3·3 per cent., and that of mercury to 204·2 tons. In furnaces Nos. 2 and 3, each furnace of 4 shafts treated in 24 hours 26·7 tons of poor small ore and pressed soot, with a consumption of 106·5 cubic feet of wood per 10 tons of ore. The cost of wages for this quantity of ore amounted to 14*s.* The production of soot amounted to 1·3 per cent., that of mercury to 117·7 tons. The loss of mercury in this furnace was 6·5 per cent. These furnaces have given very good results, and fine ores should therefore as a rule be treated in them, unless they have to be worked in long-bedded calciners on account of the production of too large quantites of flue-dust.

The Extraction of Mercury in Reverberatory Furnaces

Reverberatory furnaces are inferior to the above described shaft furnaces in every respect. They are employed for small ore which yields too much flue dust when treated in shaft furnaces; also for coarser ore which decrepitates readily in the shaft furnace, and for ores that readily sinter. The first reverberatory furnaces were constructed in 1842 by Alberti in Idria. The last of these Alberti furnaces was discontinued in the year 1887. In 1871, the first iron-clad reverberatory furnaces heated from beneath the hearth were built at Idria by Exeli, which were followed in the year 1879 by Czermak's long-bedded calciners. The latter were re-modelled in 1888 by Spirek, and thus received their present form. If the nature of the ore necessitates the employment of reverberatory furnaces, long-bedded calciners should as a rule be employed. The Alberti furnace, the Exeli reverberatory furnace, and the reverberatory furnace at present employed in Idria will be considered in some detail. Reverberatory furnaces are not in use either in Spain or in America.

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[1] Mitter, *op. cit.*

The Alberti Furnace

The construction of these furnaces is shown in Figs. 235 to 237, which represent two furnaces lying side by side. *a* is the firegrate, *f* the hearth 13 feet 6 inches long and 7 feet 3 inches broad; *p* is the working door, *c* a chamber into which the distillation residues can be emptied, *d* the charging hopper provided with a slide. The gases and vapours first pass into the brick chambers *g*, then through the iron pipe *h*, 27½ inches in diameter, into the brick chambers *i*, after which they traverse the chambers *k*, *l*, *m*, pass from the latter by means of the iron pipes *n*, into the chambers *o*, and lastly into the stack. In the latter there are compartments *p*, *q*, *r*, which the gases are compelled to traverse before being allowed to escape, which they do through the openings *s*. Water is allowed to trickle upon the iron pipes; *t* are manholes. The quicksilver collects in reservoirs built in the brickwork of the chambers. The soot deposits in the iron pipes and in the chambers, and is removed from them from time to time. In this furnace, ore fines with 1 per cent. of mercury and also soot were treated. The furnace received charges

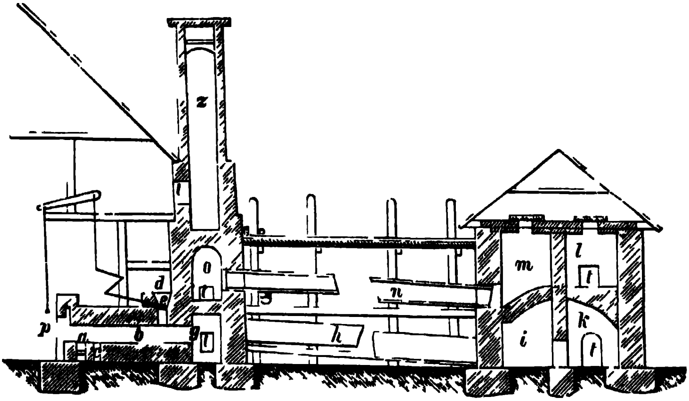


Fig 2

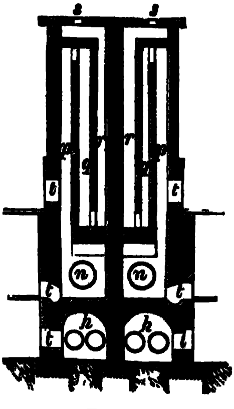


Fig 236.

of 1·1 tons, three of which were always in the furnace at the same time. These charges were drawn and pushed forward every 4 hours. In 24 hours, 6·6 tons of ore were treated with a fuel consumption of 106 cubic feet of wood, or of from 0·6 to 0·7 ton of lignite. The loss of mercury amounted to 14·80 per cent. when treating coarse small ore containing 0·4 to 0·6 per cent. of mercury There were 12 of these furnaces in Idria, which have been, as mentioned above, replaced by the iron-clad calciners.

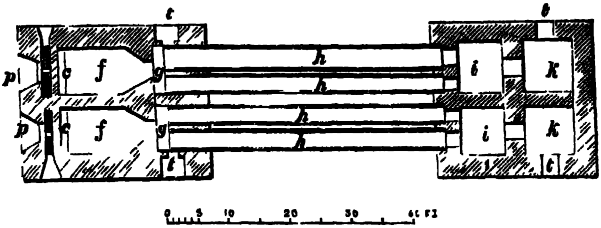
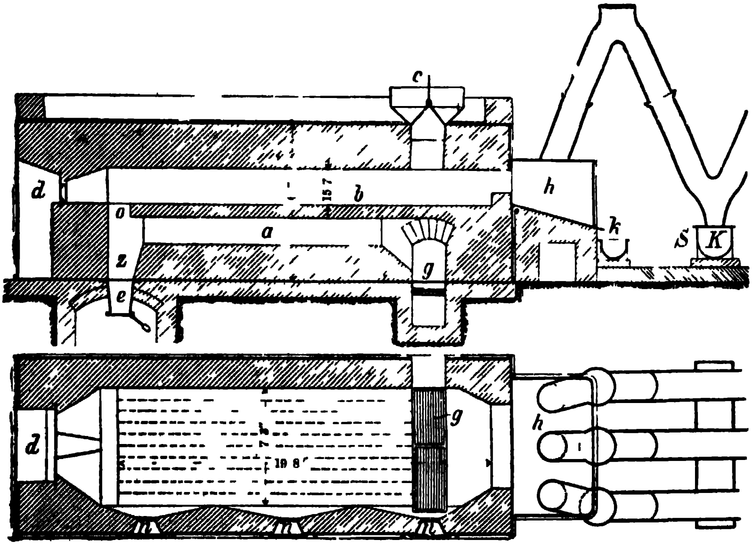


Fig. 237

Iron-clad Reverberatory Furnaces

The first of these iron-clad long-bedded calciners were built in 1871 by Exeli, and they were used up to 1877 for treating the rich soot residues and ores. The construction of this furnace is shown in Figs. 238 and 239, in which *g* is the grate; the flame traverses first the flues *a* beneath the bed of the hearth, and then passes through the aperture *o* and over the hearth *b*, 20 feet long and 7 feet 3 inches broad. After having passed over the latter, the products of combustion, together with the other gases and vapours, enter the cast-iron box *h*, cooled by a stream of water, the floor of which is steeply inclined and covered with cement. The quicksilver, which condenses in it in considerable quantity, collects in the pan *k*. The gases and uncondensed vapours pass into 3 rows, lying side by side, of cast-iron Y-shaped pipes 18½ inches in diameter, which are provided with cast-iron boxes *S* for the collection of soot and mercury. From the pipes the gases enter 2 brick condensing chambers, and from the latter they pass into a system of flues common to all the chambers, and thence into the stack; *d* and *n* are working doors; *c* is the charging hopper. The distillation residues are dropped through the opening *o* into the pocket *z*, and drawn off at *e*. This furnace, which treated rich materials, namely ores containing 3 to 10 per cent. of mercury. and soot residues, put through in 24 hours from $2\frac{1}{2}$ to 5 tons of ore according to their contents of mercury, with a consumption of 106 cubic feet of wood. The loss of mercury amounted to 10 to 12 per cent.

This furnace was superseded in 1888 by the Czermak furnace as altered by Spirek, which is the furnace now employed. Its construction is shown in Figs. 240 to 243, Fig. 240 showing a longitudinal section, 242 a plan, 241 a cross-section on the line *A-B*, and



FIGS. 238 and 239.

243 a cross-section on the line *C-D*. Two furnaces are united in one block. The furnace stands on a dish of riveted sheet-iron; *a* is the firegrate; the flame passes in flues *b* under the bottom of the furnace, and then passes over the hearth *c*, which is 18 feet long and 7 feet 6 inches wide, and is built of tiles 1·2 to 1·6 inches thick. The gases and vapours pass through 3 openings into the condensing appliances, which consist of a series of tubes made of glazed stoneware followed by wooden chambers; *t* is the charging hopper. The distillation residues are drawn off at *z*. The condensers, consisting of Y-shaped tubes, are similar to those in the Idrian furnaces and the shaft furnaces, except that there are only 4 rows of tubes with 6 tubes in each. The construction of the condensers and the method of connecting them with the furnaces and the dust chambers is shown in

Figs. 244 and 245. The method of connecting this furnace, each pair of which forms one block, with the condensers and the dust chambers is shown in Fig. 245, in which *O, O* are the furnaces, and *a, a* are the outlet pipes through which the gases and vapours from the furnaces enter the distributing pipe *b*; *c, c* are the vertical condensing pipes, and *d, d* the dust chambers. The latter are made of boards 2 inches thick, and are supported on brick pillars *p*, the floor of the chambers being protected by a layer of Portland cement 2·4 to 3·2 inches thick. The floor beneath the condensers is concreted, there being gutters in the concrete by means of which the wash-water is run into sumps.

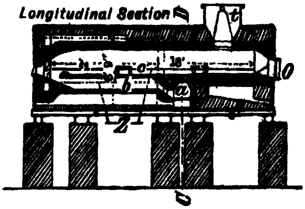


FIG. 240.

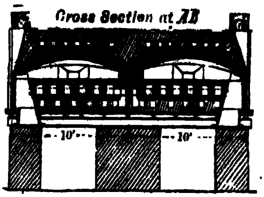


FIG. 241.

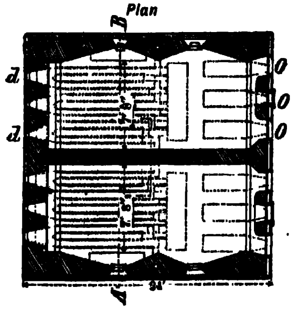


FIG. 242.

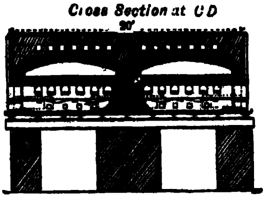
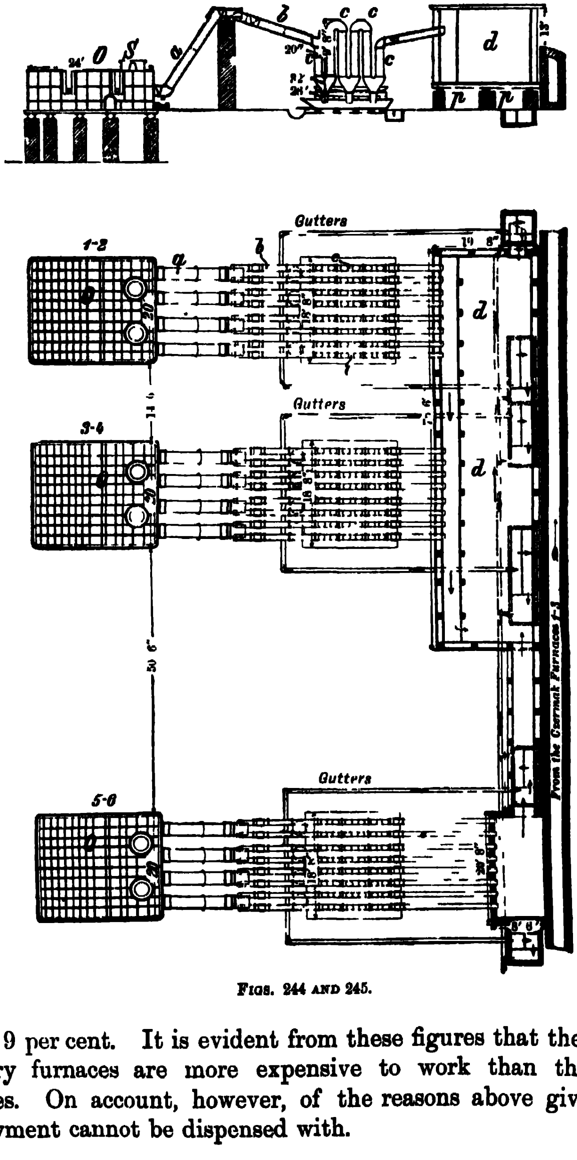


FIG. 243.

The latter are also built of concrete and are cemented twice a year. The condensers are cleaned out every fortnight. These calcination furnaces serve for the treatment of fine ores making very much dust, and of ores that decrepitate in shaft furnaces, it being impossible to treat these classes of ore in any form of shaft furnace. The residues are drawn out and new ore is charged every 2½ hours. These furnaces treat in 24 hours 6·6 tons of poor ore and soot. The consumption of fuel amounts to 148 cubic feet of wood per 10 tons of ore. A pair of furnaces are served by 3 men in an 8-hour shift, viz., one fireman, one labourer for wheeling in ores, and one for removing the residues; wages vary from 20*s.* to 22*s.* per 10 tons of ore. The production of soot amounts to 1·9 per cent. The loss of mercury

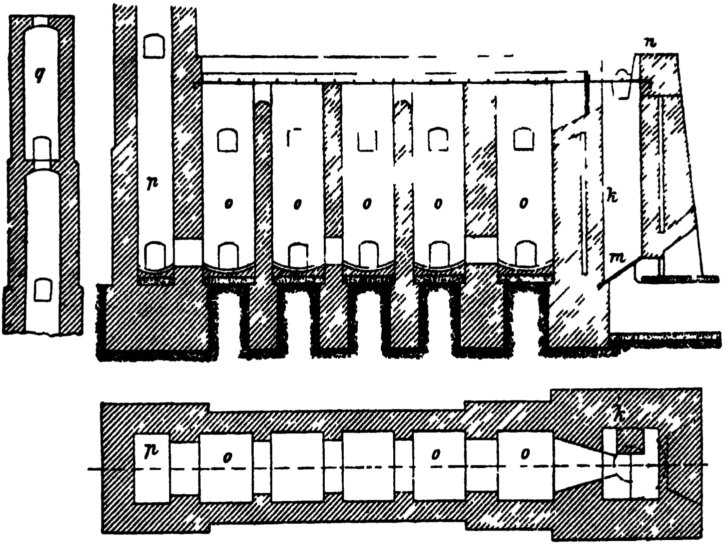


FIGS. 244 AND 245.

is 8 to 9 per cent. It is evident from these figures that these reverberatory furnaces are more expensive to work than the Idrian furnaces. On account, however, of the reasons above given, their employment cannot be dispensed with.

Extraction of Mercury in Shaft Furnaces Proper

Shaft furnaces proper, or those furnaces in which ore and fuel come into direct contact, work continuously, and when carbonised fuel is employed have the advantage, as compared with externally fired furnaces, that the production of mercurial soot (on account of there being no carbonaceous soot present in the products of combustion) is a very small one, in consequence of which the direct production of mercury is comparatively high. They should, therefore, be used as a rule for the treatment of lump ores in those cases in which carbonised fuel, especially charcoal, can be cheaply obtained. They are suitable both for lump ores and for bricks made of small ore; they are used with satisfactory results at Idria, where the externally fired furnaces of Exeli and Langer have been converted into true shaft furnaces by bricking up their fireplaces. In addition to these, shaft furnaces have been used at Ripa, Castellazara and Valalta in Italy, as also at St. Annathal, near Neumarktl in Carniola. At Almaden they have only been used experimentally (Pellet furnace). The oldest shaft furnace is the so-called Hahner furnace, which was introduced in the year 1849 in Idria, where it was in operation up to 1852. The construction of the Idrian Hahner furnace is shown in Figs. 246 to 248, in



Figs 246—248.

which *k* is the shaft 36 feet high and 4 feet in diameter; *m* is an inclined movable grate upon which the column of ore rests. In order to remove the distillation residues, a certain number of the firebars can be withdrawn, so that the former can drop into waggons placed below the grate; *n* is the charging hopper; *o* are brick condensing chambers with concave floors inclined to one side in order to enable the mercury to run off. The chambers are provided with a roof of cast-iron cooled with water; they are 18 feet 6 inches high, 6 feet broad, and 4 feet 3 inches long; *p* and *q* are sections of the stack, which is 6 feet 3 inches by 4 feet in plan. Alternate layers of ore and charcoal are charged into this furnace. At intervals of 1½ hours the distillation residues are removed and a corresponding quantity of fresh ore charged. This furnace was replaced by the Valalta furnace, to be presently described.

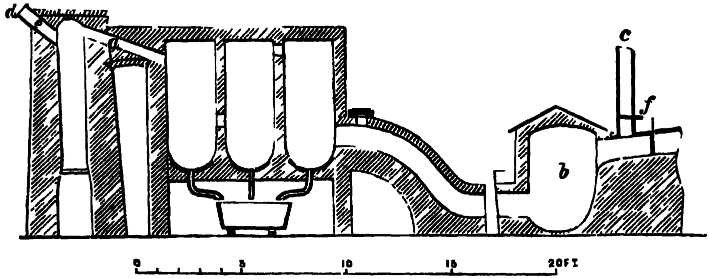


FIG. 249

The furnace at Castellazara, near Santafiori in Tuscany, is shown in Fig. 249. The shaft has a height of 7 feet 3 inches above the grate, its diameter being 15¾ inches. The distillation residues are withdrawn through a lateral opening above the grate. The gases and vapours traverse 3 condensing chambers one after the other, the floors of which are formed of cast-iron pans. The mercury that settles in the latter is drawn off by means of pipes provided with cocks, into waggons placed beneath them. From the last condensing chambers, the gases and vapours enter another chamber *b*, and thence pass to the stack *c*. Ores were treated in this furnace which contained from 0·3 to 0·4 per cent. of mercury.

The furnace of Valalta in Venice,[1] which was used also at Idria from 1868 to 1878, is provided with wooden condensing flues cooled by water. Its construction is shown in Fig. 250; *a* is the shaft 21 feet 4 inches high and 4 feet broad. The gases and vapours pass through the chambers *b* and *c* into the wooden pipe *d*, 3 feet 3 inches broad and 50 feet 6 inches long, thence into the chambers *e*, *f* and *g*, from the latter of which it passes into the upper wooden pipe *h*, also cooled by water, which possesses the same dimensions as the lower pipe. From this it enters the chamber *i*, and thence the stack *k*. The pipes consist of a number of short conical pipes set one into the other. The draft is produced by means of a water trompe *p*, connected with the stack, in the water tube *o* of which the last portions of mercury are collected. These furnaces treat in 24 hours 9 tons of ore containing 0·45 per cent. of mercury, with a consumption of fuel equal to 20 per cent. The loss of mercury is said to amount to 22·3 per cent.

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[1] *Oesterr. Zeitsch.*, 1862, p. 195; *Berg. und Hütt. Ztg.*, 1864, p. 284; 1868, p. 32; *Eng. and Min. Journ.*, 1872, vol. xiv., Nos. 11 and 12.

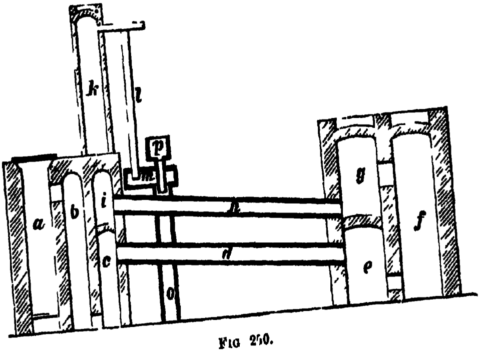

Fig 250.

The furnace at St. Annathal, Carniola,[1] is shown in Fig. 251. It is square in horizontal cross section, 4 feet by 4 feet, its height amounting to 30 feet 6 inches. The gases and vapours traverse 2 rows of cast-iron pipes contained in a cooling chamber *k*, and thence pass through wooden pipes *f* into a chamber *g*. The latter is connected to a water trompe which produces the requisite draft. The greater part of the mercury is collected in the box *d*, and the distillation residues are removed through man-holes *m*, of which there are three. The ore contains 0·8 per cent. of mercury; it remains for 46 hours in the furnace, which takes 23 charges of 11·2 cubic feet of ore and 1·76 cubic feet of charcoal. The distillation residues

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[1] *Karnthener Zeitsch.*, 1877, p. 332.

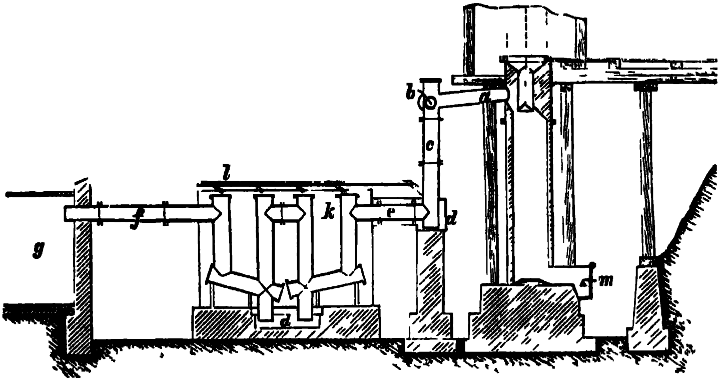


FIG 251

are removed from the furnace every two hours, when a corresponding quantity of fresh ore is charged.

The furnace built at Idria in 1888, which was replaced in 1892 by the new Novak shaft furnace, on account of its unsatisfactory results, is shown in Figs. 252 to 254. *A* is the shaft *B* being the shaft lining, *C* the retaining wall, *D* the iron casing, *G* are cast-iron columns which support the shaft; *E* is the charging apparatus. *F*, *F* are openings through which the distillation residues are drawn out of the furnace. The gases and vapours pass through the tube *H* into the Czermak condenser, which consists of Y-shaped tubes *J*, made of clay. The condensed mercury collects in the vessel *L*, which is filled with water. From the condensing tubes the gases and vapours pass into the brick chambers *K*.

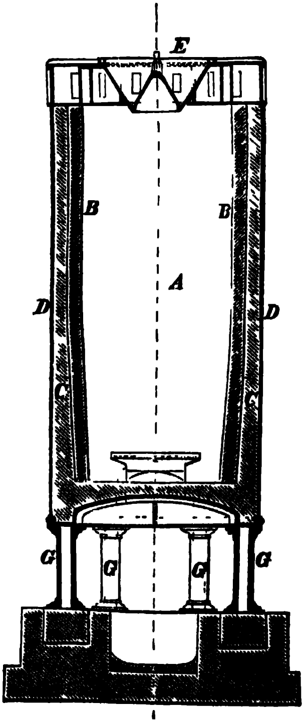


FIG 252.

This furnace was replaced in 1892 by the very successful new Novak furnace. This is rectangular in cross-section and has four openings for the removal of the residues. The retaining wall is 24 inches thick, the inner wall 8 inches. The construction and

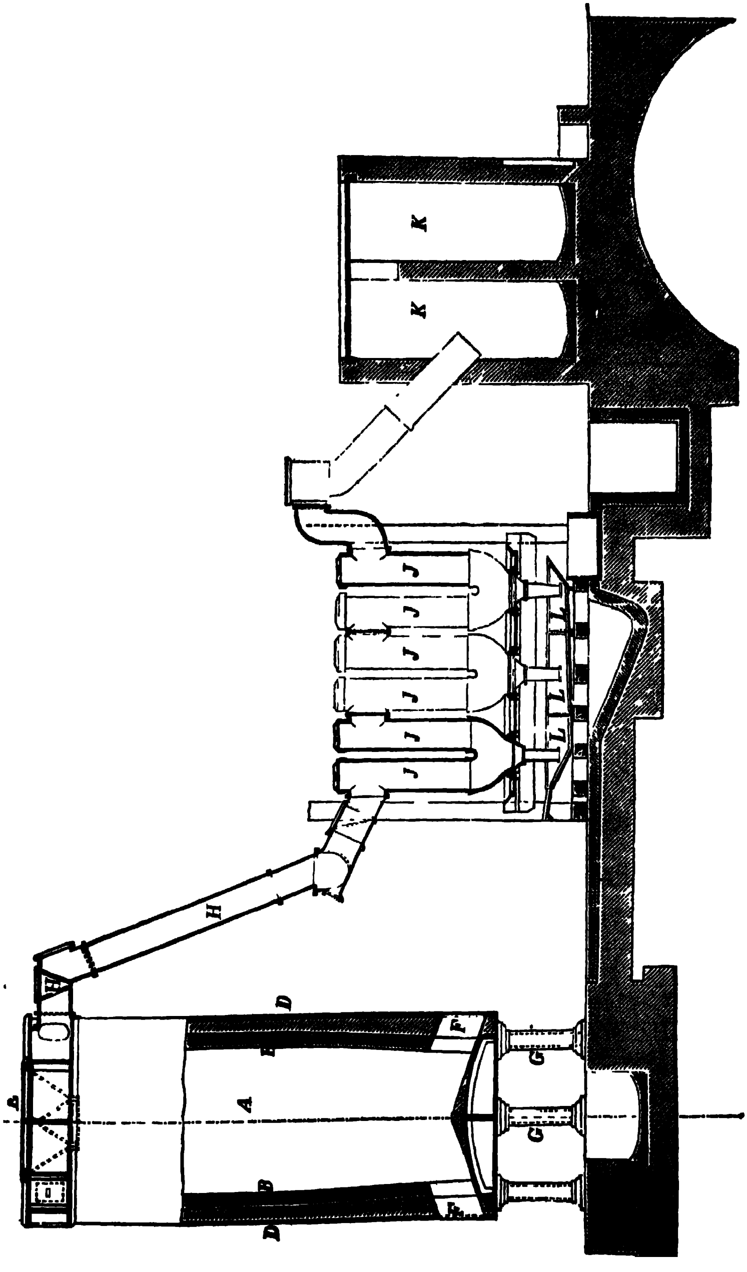


FIG. 253.

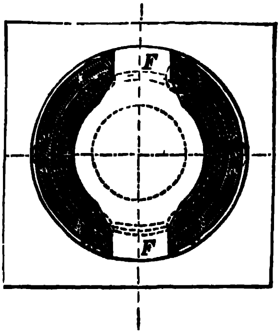
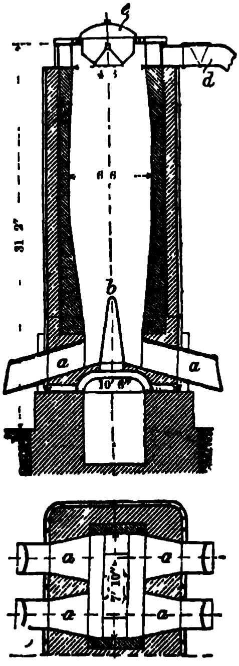


FIG. 251.

dimensions are shown in Figs. 255 and 256. Three of these furnaces are united to form a block; *a* are the openings for drawing off the residues, *b* is a roof-shaped ridge on the bottom, pierced with numerous small openings. Through the latter, air enters from the bottom of the furnace and, thus heated, passes into the furnace through the above-named holes; *c* is the charging hopper, *d* the escape pipe for the gases and vapours, which thence enter the stoneware condensers and pass onwards into dust chambers. In this furnace poor ore down to 0·67 inch mesh is treated, together with pressed soot; the furnace, which is charged every two hours, will put through 12·1 tons of ore in 24 hours. For 10 tons of ore 1·6 tons of charcoal are consumed. 4·2 men are employed for two shaft furnaces on an 8-hour shift. The cost of wages per 10 tons of ore amounts to 13*s.* 4*d.* The production of soot amounts to 0·5 per cent., the loss of mercury to 7 to 8 per cent. The condensers, as in the other Idrian furnaces, consist of Y-shaped tubes of stoneware cooled by water. They are oblong in cross section, are 0·8 inch thick, and are supported in wooden frames. The various pipes are joined together by means of cement. The lower contracted branches dip for about 2 inches into water contained in cast-iron boxes, which are lined with cement. For each furnace there are 4 rows of tubes, with 6 tubes in each. The gases and vapours enter at a temperature of 200° to 300° C., and finally escape at a temperature of 8° to 12° C. From 4·4 to 6·6 gallons of water are used per hour per furnace for cooling purposes. When poor coarse ore is being treated, the condensed mercury is swept out every 14 days from the condensers into the boxes lying beneath them, but every 4 or 5 days when pressed soot is being treated. The mercurial vapours



FIGS. 255 AND 256

escaping from the stoneware pipes are condensed in chambers constructed of wood and divided by partition walls into several divisions, the wooden walls being made air-tight by groove and tongue joints. The construction of the condensers, the method of connecting them with the shaft furnaces, and the dust chambers are similar to those described on page 312. The stoneware condensers introduced by the chief works manager, Mitter, have completely replaced the iron condensers which lasted only 1 to 1½ years, whilst the stoneware condensers last for any length of time, and cost only one-third as much as the iron condensers. They are made in Floridsdorf, near Vienna, at the factory of Lederer and Nesseny.

THE EXTRACTION OF MERCURY IN RETORT FURNACES

The extraction of mercury in retort furnaces is not to be recommended on account of the injurious effects of the mercury vapours upon the workmen engaged. The losses of mercury are moreover no less than in modern shaft and reverberatory furnaces, their only advantage being that their first cost is less than that of the latter furnaces. On the other hand, the working costs are higher on account of their smaller capacity. The material of the vessels and of the condensers is cast-iron. These furnaces have been used for a while in Idria and California, but are probably nowhere in use at the present day. At Idria the furnace of Von Patera was used for a while experimentally. Its construction is shown in Figs. 257 and 258.[1] *A* is the muffle, 23½ inches broad, 29½ inches long and 9 inches high; *c* is the condenser made of sheet iron provided with an inclined floor along which the condensed mercury runs towards the pipe *d*, through which it enters the collecting pan placed beneath it. From this condenser the gases and vapours pass through an iron pipe into a system of clay pipes and thence into the stack; *f* and *h* are openings for cleaning out the condenser, which can be closed by means of clay plugs; *g* is a

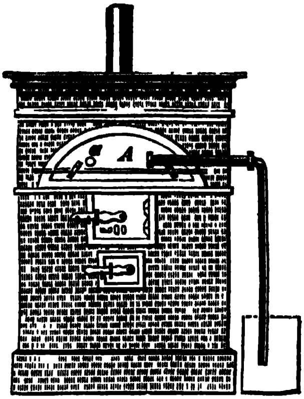


FIG. 257.

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[1] *Oesterr. Zeitschr.*, 1874, p. 291; *Berg. und Hütt. Ztg.*, 1874, pp. 91, 419.

short branch pipe in which a gold-leaf is suspended; in normal working, this may not show any coating of mercury; *i* is a short branch into which a thermometer can be inserted. The air required for oxidation is introduced through openings *a*. The charge of the muffle is said to have amounted to 1 cwt. of ore. The output, when ores containing 1·5 to 3·6 per cent. of mercury were treated, is said to have amounted to 90 per cent., whilst in the furnaces at present in use at Idria, the output amounts to 91·75 per cent.

At the Missouri Mine, near Pine Flat, and at the Lost Ledge Mine, in California, retort furnaces were used.[1] The furnaces at the Missouri Mine contained either two or three cast-iron retorts 9 feet 6 inches long, 12·5 inches high and 19 inches broad These were charged with 2½ cwt. to 3½ cwts. of ore, containing from 1 to 2 per cent. of mercury. In 24 hours, 10 cwts. to 1 ton of ore were treated. The consumption of fuel per furnace was about 3½ cords of wood per 24 hours on the average. The gases and vapours were conveyed through an iron pipe into iron boxes open below, which dipped into an iron tank filled with water. In this tank, which was 3 feet long, 24 inches broad and 24 inches high, the mercury was condensed. The furnaces and condensing appliances at the Lost Ledge Mine were similar except that the retorts, of which there were three in a furnace, were smaller, being only 5 feet long and holding only 183 lbs. of ore. They were charged every 4 hours. In 24 hours such a furnace treated about 1½ tons of ore.

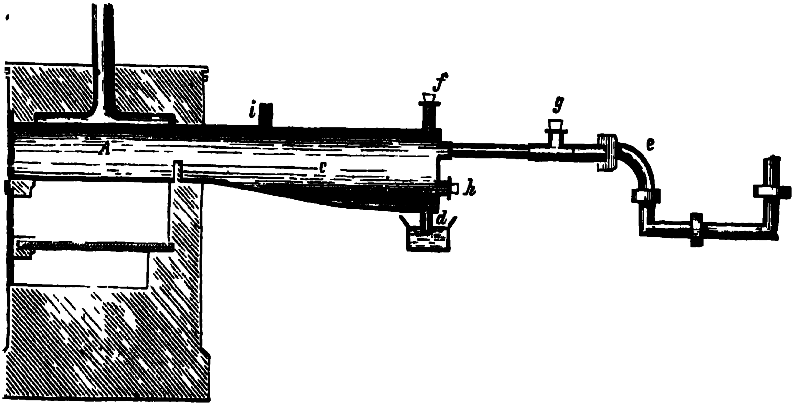

FIG 2[illegible]8

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[1] *Trans. Am. Inst. Mng. Engrs.*, 1875, vol. iii., p. 276.

THE EXTRACTION OF MERCURY BY HEATING CINNABAR WITH LIME OR IRON IN THE ABSENCE OF AIR

This method of mercury extraction has the advantage that the vapours of that metal are obtained in a concentrated condition, and are therefore readily condensed. The first cost of the furnace and condensers required is also lower than of those needed for the extraction of mercury by heating cinnabar in the air. On the other hand, the residues contain more mercury, so that the output is thus reduced and the process gives no better results even with the most careful work than can be obtained with the other method. The costs of working are very high, in consequence of the necessity for employing fluxes and for previously crushing the ore, as also on account of the high consumption of fuel and the small output of the retorts. The costs of repairs are also high in consequence of the retorts becoming rapidly destroyed. The greatest disadvantage, however, may be considered to be the injurious effect of the fumes of mercury upon the workmen. Generally speaking the process is unsuitable for poor ores, and for rich ores it is in no way cheaper than the other methods of treatment, whilst for hygienic reasons it cannot be recommended even for rich ores. It should therefore only be employed when small quantities of very rich ores or soot are to be treated, and should be condemned for working rich ores upon a larger scale. The retorts in which the cinnabar is decomposed were first pear-shaped or bell-shaped, and were made of clay or cast-iron; later cast-iron alone was employed, and the retorts received the shape of those employed in the distillation of coal-gas. The condensers, which were formerly made of clay at some works, are now also made of cast-iron. The flux required for decomposing the cinnabar should as a rule be quicklime; iron or hammer-slag have only been used exceptionally for decomposing the ore. Lime acts upon cinnabar at a red heat, as shown by the following equation:—

$$4HgS + 4CaO = 3CaS + CaSO_4 + 4Hg,$$

the action of iron being as follows:—

$$HgS + Fe = FeS + Hg.$$

The process has been employed in California, in Idria, in the Rhenish Palatinate and in Bohemia, and is still in use at present at Littai in Carniola, and at Monte Amiata in Tuscany. It was given up in California on account of the above objections in the year 1850, and from that date up to 1860 was only used experimentally.[1] It was used in Idria for soot and rich ores up to 1882. At Moschellandsberg, in the Rhine Palatinate, and at Horzowitz, in Bohemia, it has been given up because the deposits found at those localities have been worked out.

At the American Mine, Pine Flat, California,[2] ores containing 2 per cent. of mercury were heated in cast-iron retorts of the shape of gas retorts 9 feet in length, 2 feet in width and 18 inches in height, in charges of 150 lbs., with the addition of 10 per cent. of lime; 500 lbs. of ore were put through in 12 hours. Even apart from the injurious effects upon the workpeople, the treatment of such poor ores in retorts must be condemned.

At Landsberg, in the Bavarian Palatinate, pear-shaped retorts were at first employed; they were 3 feet 3 inches in length, with a maximum diameter of 18 inches, and 40 to 60 of them were placed in 2 rows in a galley furnace. The condensers were pear-shaped vessels of clay 16 inches long and 9½ inches maximum diameter, which contained a certain quantity of water. The charge consisted of 44 lbs. of rich ore, 44 lbs. of poor ore, and 18 to 20 lbs. of burnt lime; such a charge was treated in from 6 to 8 hours. One part by weight of mercury was obtained from 80 to 120 parts of ore according to the richness of the latter, with a consumption of 20 to 30 parts of coal. In 1847 Ure introduced retorts of the shape of gas-retorts. From these retorts the vapours were passed through iron tubes into boxes half filled with water, in which the mercury was condensed. The tubes dipped for 2 inches below the surface of the water. The charge of ore for a retort amounted to 5 cwts., and it was worked off in three hours.

At Horzowitz, in Bohemia,[3] the ore was mixed with hammerslag and treated in bell-shaped vessels. The charge was 55 lbs. of ore and 27 lbs. of hammerslag, which required 36 hours for their treatment.

At Idria, in Carniola, a furnace was introduced by Exeli in 1869 and worked up to 1882 for the purpose of treating finely crushed ores and soot. This furnace,[4] the construction of which is shown in Figs. 259 to 262, contained two cast-iron retorts, *a*, 7 feet 4 inches long, 2 feet 3 inches broad, and 1 foot 1 inch high, which were closed at the back by means of a cast-iron cover coated with clay; *b* is the fire-grate. The vapours escaped through horizontal tubes *t*, 6¼ inches in diameter, into vertical tubes, *c*, of the same diameter and 5 feet in height, which were provided with discs for cleaning them out, and which opened into an inclined collecting tube, *d*, 9½ inches in diameter. The vertical condensing pipes and the collecting tube are contained in a wooden cooling box filled with water. The condensed mercury flows through the inclined tube *d*, into the tube *z*, and from the latter into a closed receiver *q*, filled with water, from which the mercury is syphoned off into the kettle *p*. The uncondensed gases pass through the middle tube *y* and the inclined tube *x* into the dust chamber and the flue; *s* is a vertical shoot through which the distillation residues can be dropped direct from the retorts into the vault *k* or into the waggons which are run into it. In these furnaces, fine ore with 10 per cent. of mercury, and soot were treated. The material was mixed with lime in the proportion of 1·5 parts of caustic lime for every part of mercury contained in the ores, and then moulded into bricks in a special press. These bricks were dried and charged into the retort, which held 108 bricks at a time, weighing altogether 300 lbs. This

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[1] Egleston, *op. cit.*, p. 112.

[2] Egleston, *op. cit.*, p. 811.

[3] Kerl, *Metallurgie*, vol. ii., p. 811.

[4] *Idrianer Festschrift*; Mitter, *loc. cit.*

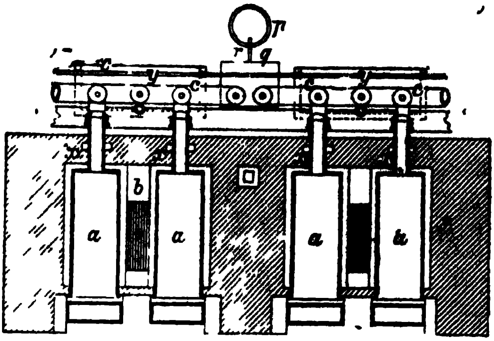

FIG. 259

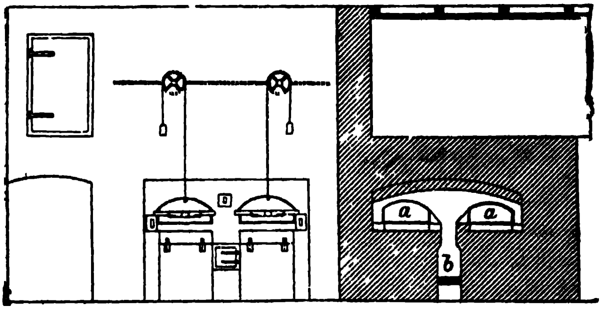

FIG. 260

charge was worked off in from 4 to 6 hours, according to the richness of the ores. The consumption of fuel per 24 hours amounted to 63·5 cubic feet of wood and 794 lbs. of lignite.

At Littai, in Carniola, where the process is still in use, a furnace very similar to the Idrian retort furnace is employed. Its construction is shown in Figs. 263 to 266;[1] *a* are the cast-iron retorts, *b* is the grate, *d* are the tubes through which the vapour passes into the condensing tubes or into the inclined tube *g*; *f* is the cooling tank,

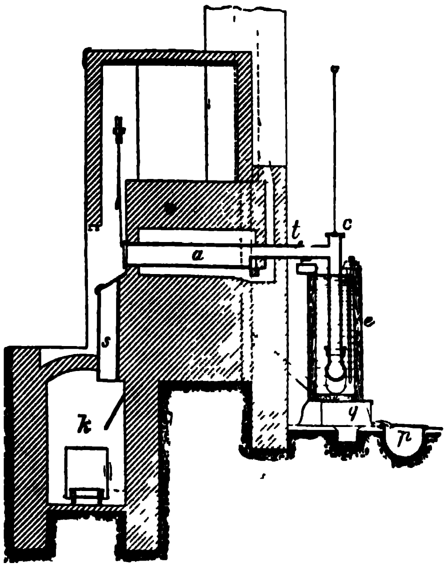

Fig. 261

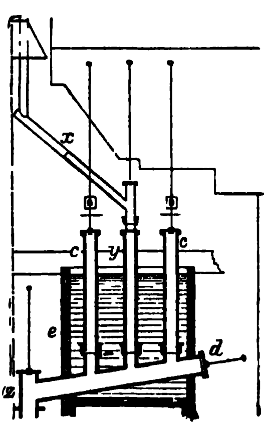

Fig. 262

i is the tube for carrying off the uncondensed gases into the tube *l*, and thence into the dust chamber *k*. The ores contain on an average 3 per cent. of mercury. They are crushed by rolls to 0·2 inch, and are charged into the retorts mixed with 5 or 6 per cent. of caustic lime, a retort taking a 2 cwt. charge, and the operation lasting 6 hours. In 24 hours 16 cwts. of ore are treated. One hundred and seventy parts by weight of fuel are used for 230 parts of ore, the fuel consisting of 80 per cent. duff and 20 per cent. pea coal. The loss of mercury is stated to amount to from 5 to 6 per cent.

At the smelting works at Siele and Connacchino at Monte Amiata,[2] ores which are dressed up to 25 to 30 per cent. of mercury

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[1] Balling, *Metallhüttenkunde*, p. 502.

[2] *Ann. des Mines*, 1888, No. 4; *Berg. und Hutt. Ztg.*, 1889, No. 10.

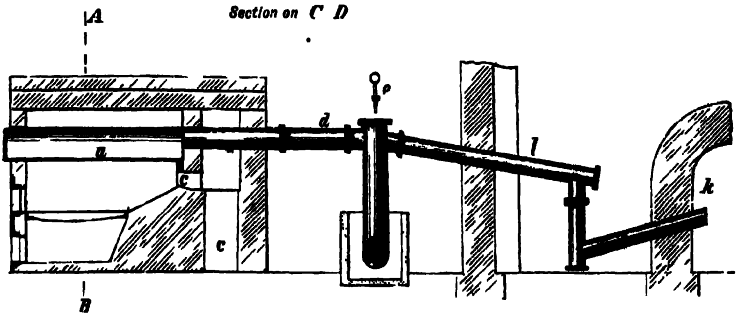

FIG 263

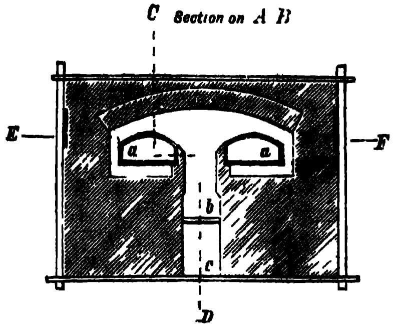

FIG 264

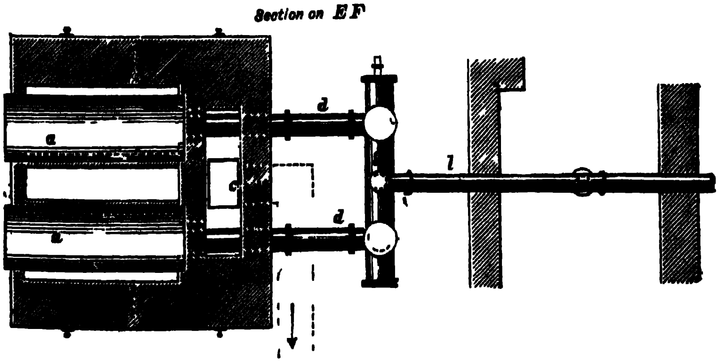

FIG 265

are heated in retorts with lime. The arrangement of the furnace, designed by Jaczinsky, is shown in Figs. 267 to 269; *a, a* are the cast-iron retorts which rest throughout their entire length upon a flue and are surrounded by the flame travelling in the direction shown by the arrows. To distribute the flame uniformly through the heating chamber, it is allowed to escape into the stack by means of three vertical flues, of which there is one above each retort. The mercury vapours escape through the cast-iron pipe *c*, 4½ inches in diameter, which is cooled with water, into a wooden box *e* filled with water, the liquid mercury running into the cast-iron receiver *f*, from which it flows continuously by the pipe *g*. The uncondensed vapours escape

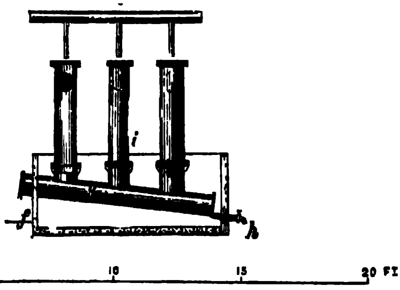

FIG. 266

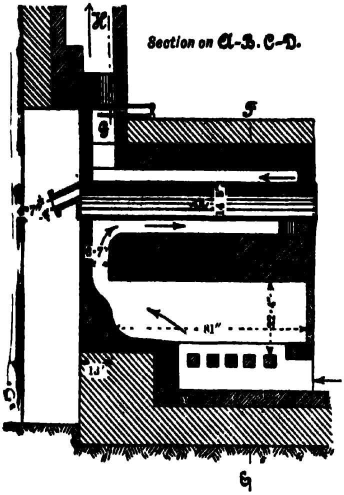

FIG. 267.

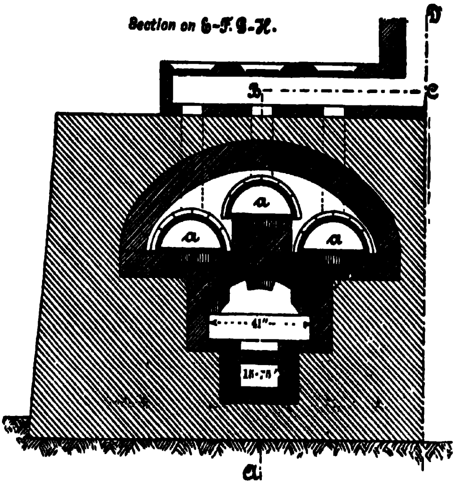

FIG. 268.

through the tube *d* into condensing chambers, in which there is a constant spray of water, and thence into the stack. The retorts hold 4 to 5 cwts. of ore, and 88 lbs. of lime, the proportion of lime being increased in the case of pyritic ores. The temperature is raised up to bright redness, and the treatment of the charge takes 7 to 8 hours. A ton of wood is used per ton of ore. When the percentage of mercury in the ores amounts to 30 per cent., the total cost of producing 2·2 lbs. of mercury amounts to 15 pence.

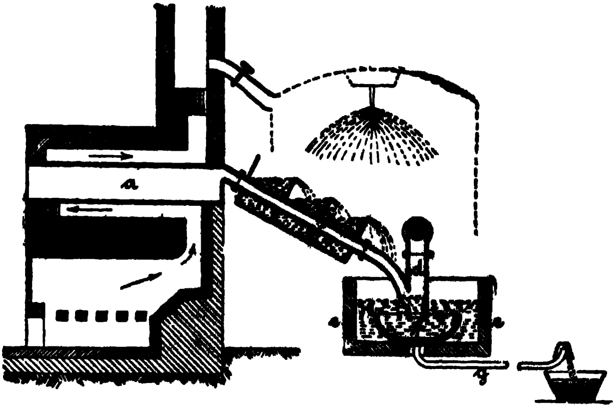

FIG. 269.

THE PRODUCTS OF MERCURY EXTRACTION

The products of the process of mercury extraction are, in addition to mercury, mercurial soot, acid water and distillation residues. The mercury is often rendered impure by mechanical admixtures, to remove which it is squeezed through canvas or leather. Mercury is sent to the market from the larger works in bottles of wrought iron with screwed stoppers. Their weight when empty amounts to 12 to 14 lbs. The flasks contain 76 lbs. of mercury in Europe and 76·5 lbs. in California. In the smaller works mercury is also exported in bags made of two thicknesses of leather.

Soot

Soot ("*stupp*"), as already mentioned, consists of the deposit upon the walls of the condensers, which often forms in considerable quantities, consisting of a mixture of finely divided mercury, mercurial compounds, carbonaceous soot produced by the distillation of the fuels, and the bituminous and other impurities of the ores. The percentage of mercury in the soot may reach 80 per cent. The composition of various qualities of soot from various sources is shown in the following analyses:—

	IDRIA.		
	1	2[1]	3
Hg	3·12	14·59	0·92
HgS	27·33	1·83	3·40
Hg_3SO_6	7·32	3·06	6·10

According to Oser,[2] soot from the condensers of the Idrian externally fired furnaces contains:—

	per cent
Mercury removable by pressure	40·95
Non-removable by pressure, and in the form of salts	9·15
Sulphuric acid	1·39
Mercuric sulphide	4·32
Carbon	3·31
Ashes	9·33
Water	31·55

The composition of soot from the condensers of the muffle furnaces of Patera, called by him *mercury black*, is shown in analysis No. 1; that of the flue soot from the flues leading to the stack and following the condensers, is shown in analyses 2 by Patera, and 3 by Teuber:—

	1	2	3
Mercury	56·30	6·42	3·12
Mercuric sulphide	0·70	2·20	31·10
Mercuric sulphate	18·99	13·07	10·80
Mercurous chloride	2·20	1·80	—
Sulphuric acid	1·10	4·80	—
Magnesia	—	1·10	—
Lime	0·76	1·20	—
Ferric oxide and alumina	trace	0·80	—
Calcic sulphate	1·04	6·30	—
Basic ferric sulphate	3·24	0·40	—
Soot and tar	3·39	29·40	24·80
Water	4·60	26·50	10·30
Ore residues	11·41	3·80	—
Ferrous sulphate	—	—	6·02
Magnesic sulphate	—	—	7·50
Sodic sulphate	—	—	1·24
Ammonic sulphate	—	—	0·54
Silica	—	—	2·20

The soot from the condensing chamber of the shaft furnace No. IX., collected in 1892, had the following composition:—[3]

Metallic mercury	65·04	=	65·04 Hg
Mercuric sulphide	6·97	=	6·00
Basic mercuric sulphate	0·20	=	0·16
Mercuric sulphate	0·12	=	0·08
Mercuric chloride	0·08	=	0·06
Mercurous chloride	0·05	=	0·04
			71·38 per cent. Hg.

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[1] Teuber, *Oesterr. Zeitsch.*, 1877, p. 123; *Dingl.*, vol. 225, p. 214.

[2] *Das k. k. Quecksilberbergwerk Idria*, Vienna, 1891.

[3] Janda, *Oesterr. Zeitschr.*, 1894, p. 268.

Alumina and ferric oxide	1·11
Ferrous sulphide	0·94
Lime	9·57
Magnesia	0·40
Sulphur trioxide	9·10
Ammonia Hydrocarbons	2·19
Soot	1·98
Silica	1·20

In 1892, samples of soot were taken at various places along the course which the gases and vapours traversed through the furnace until they reached the stack delivering them into the atmosphere, and were examined for their contents of moisture and mercury. The results of the analyses are shown in the following table. In this No. 1 was taken from the flue of the shaft furnace, Nos. 2 and 3 from the condensing chamber of the Czermak furnaces, No. 4 from the flue of one of the Czermak furnaces, Nos. 5 and 6 from the flue leading to the fan, and Nos. 7 and 8 from the main stack:—

Number of the Sample.	Moisture per cent.	Percentage of Mercury as			Total Mercury per cent.
		Salts.	Cinnabar.	Metal.	
1	14·8	0·20	18·83	43·17	62·20
2	—	3·04	6·75	22·01	31·80
3	85·8	trace	4·00	18·00	22·00
4	40·2	–	6·40	21·80	28·20
5	—	0·16	9·68	3·76	13·60
6	—	0·75	9·24	4·16	14·15
7	35·0	0·69	13·75	0·86	15·30
8	65·9	0·16	9·35	3·49	13·00

The proportion of mercury respectively contained by the salts, cinnabar, and metal of the various samples was therefore distributed as follows:—

Number of the Sample.	Percentage of the total Mercury present in the form of		
	Salts.	Cinnabar.	Metal.
1	0·32	30·28	69·40
2	9·55	21·23	69·22
3	trace	18·18	81·81
4	—	22·69	77·30
5	1·17	71·18	27·65
6	5·30	65·30	29·40
7	4·51	89·87	5·62
8	1·23	71·92	26·84

Soot from Almaden has the following composition:—[1]

	Soot from Clay condensing tubes. Per cent.	Soot from Iron condensing tubes. Per cent.
Mercury as metal	66	44
Mercurous chloride	18	3·3
Mercuric sulphide	1	6·3
Ferrous sulphate	—	23·5
Aluminic sulphate	—	14·5
Potassic sulphate	—	
Ammonic sulphate	3·5	—
Calcic sulphate	1·	0·9
Carbon	5	4·8
Sulphuric acid	2·5	—
Water	2·5	—

The Treatment of Soot

Mercury is extracted from soot, firstly by *pressing* the latter, whereby a considerable portion of mercury is made to flow out, and secondly, by treating the residues thus obtained, either together with ores or by themselves, in distillation furnaces. Soot is pressed either by hand or by machinery. To promote the removal of the mercury, lime or ashes are added to it. The best method of pressing soot consists in treating it in pans provided with stirrers or in cylinders, which, on a large scale, are driven by machinery.

At Almaden,[2] the soot is worked upon an inclined wooden surface with hoes until no more mercury flows off. The residues that are then left are moulded into bricks and treated with the ores. This rubbing up of soot in the above way was also carried on at Idria and in the Californian Works, but on account of its being injurious to the health of the workmen, has been given up for a considerable time. For example, at the Redington Mine, in California,[3] soot was treated in this way, the residues being heated in retorts with lime. At New Almaden the soot was first treated as above.[4] As soon as no more mercury could be extracted in this way, lime was added and the rubbing continued, when another portion of mercury was obtained.

At Idria, the soot presses designed by Exeli are at present employed. Their construction is shown in Figs. 270 and 271. They consist of iron cylinders with a V-shaped bottom. The diameter of the cylinder in the clear amounts to 4 feet, the height to 17 inches. Through the middle of the cylinder passes a vertical shaft *w*, to the upper end of which are attached 4 arms at right angles to each other, these arms being 11½ inches above the bottom of the apparatus. To these arms are bolted knives *z*, 3 inches broad and 0·3 to 0·4 inch thick. To the bottom of the apparatus, 7 or 8 vertical knives, *o*, of the same dimensions, are so attached, that when the arms revolve the movable knives *z* pass close to the fixed knives, and thus press the soot together and force it upwards. In the lowest portion of the apparatus there are 25 apertures of 0·4 inch diameter, through which the mercury flows away as fast as it is pressed out. These openings readily become stopped up and must be kept open during the operation by means of a stout wire. It is important that the bottom ends of the movable knives should touch the bottom of the apparatus, and when they are worn they should be immediately replaced by new ones, otherwise a layer of soot forms upon the bottom of the apparatus which stops up the holes through which the mercury should escape. When the shaft is set in motion the mercury is squeezed out from the soot mixed with lime, and collects in the lowest portion of the bottom, whence it runs through the above-named openings into the receiver *g* standing beneath it. The soot residues are also collected in a box placed beneath the apparatus. The weight of a charge of soot depends upon the amount of mercury and of moisture contained in it, and varies between 44 and 110 lbs. The quantity of lime to be added depends upon the same conditions. More must be added to soot rich in mercury than to poor soot, the amount varying between 17 and 30 per cent. of the weight of the soot; the lime is not added all at once, but in small quantities during the course of the operation. The speed of revolution is at first low, and rises gradually from 12 to 40 revolutions per minute. After 20 minutes the knives ought to commence to lift the soot from the bottom of the apparatus and to throw it up. Generally speaking, the soot is sufficiently well pressed when the residues begin to agglomerate into pellets. The time required for pressing depends upon the richness of the soot. In the case of rich material it lasts from 1¼ to 1⅝ hours. By this operation from 70 to 80 per cent. of

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[1] *Berg. und Hütt. Jahrb. der k. k. Montanlehranstalten*, Vienna, 1879, p. 81.

[2] *Ibid.*, vol. xxvii., p. 46.

[3] Egleston, *op. cit.*, p. 850.

[4] Egleston, *op. cit.*, p. 834.

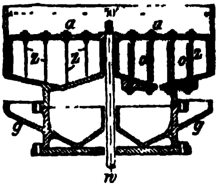

FIG. 270.

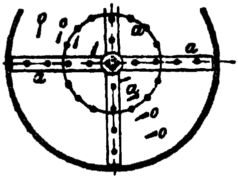

FIG. 271

the mercury contained in the soot is separated, the remainder of the mercury, which amounts on the average to 14 to 20 per cent. of the weight of the residues, being obtained by distilling these residues together with ores. A sample of pressed soot from shaft-furnace No. VIII., taken in December, 1892, contained :—[1]

	Per cent.
Mercury in combinations soluble in hydrochloric acid	0·17
Mercury as cinnabar	2·96
Metallic mercury	14·98
Total	18·11

At New Almaden, the soot was treated from 1873 to 1887[2] in hemispherical cast-iron pans 36 inches in diameter, for three-quarters of an hour, by constant stirring with boiling water and wood ashes. The quantity of the latter amounted to half of the volume of the soot. The quicksilver that separated out was drawn off by means of a syphon through the bottom of the pan. The residues were dried and treated together with the ores in distillation furnaces.

A cast-iron pan was also employed at the Manhattan Works. Above the pan, of a capacity of 120 gallons, a vertical shaft was carried by a wooden frame. To the bottom end of the former, horizontal wooden arms were attached carrying iron tines. The soot was mixed with ashes and lime, and the mass was stirred for 20 minutes, at the end of which time all the mercury that could thus be removed had been extracted, and the mass was completely dry. The mercury was drawn off by means of a pipe at the bottom of the pan and the residues were distilled in retorts. At present, at New Almaden, wet and semi-fluid[3] soot is stiffened by mixing with half its volume of wood ashes upon a rectangular asphalted floor, 20 feet long and 9 feet broad, which is hollowed and at the same time inclined to one of its shorter sides; a paste is thus obtained which is transferred in buckets to the press, consisting of a cast-iron pan of 40 inches diameter at its upper wider end. In it there stands a vertical shaft with 4 plough-shaped stirrers. The mass is stirred for 1½ hours, the stirrers making 40 revolutions per minute, at the end of which time no more mercury flows out. The mercury is drawn off by means of a syphon at the bottom of the pan. The residues are drawn off into a box standing below the pan, through a larger opening in the bottom of the pan, which is kept closed during the course of the operation by means of a valve. 14 per cent. of the mercury contained in the soot remains in the residues, which are treated by distillation; it is impossible to remove the whole of the mercury from the soot by pressing alone.

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[1] Janda, *op. cit.*, p. 269.

[2] Egleston, *op. cit.*, p. 884.

[3] Egleston, *op. cit.*, p. 882.

The residues contain, according to the method of pressing employed, variable quantities up to 40 per cent. of mercury. For example in Idria[1] the residues obtained by pressing in the years 1890 to 1892 contained 14·89 per cent. of the entire output of mercury. In order to extract this mercury from the residues, the latter must therefore be subjected to a further treatment. This consists in distilling the residues in the same way as the ores in the various furnaces used for ore treatment, as a general rule mixed with ore, and more rarely by themselves. At Almaden, the soot residues are moulded into bricks, and are treated with the ores. At Idria, the residues were treated for a while in retort furnaces; now, however, they are distilled with the ores in shaft and reverberatory furnaces. When soot residues were distilled in retort furnaces, a resinous substance, known as "soot fat" (*stupp fett*), condensed in the receivers; it consisted chiefly of hydrocarbons mixed with only small quantities of mineral substances. According to G. Goldschmidt and M. von Schmidt, 32 kilos of *stupp fett* only contained 150 grammes of mineral matter, which latter contained 70·35 per cent. of mercury, partly as metal, partly in combination with sulphur together with iron, manganese, alumina, lime and magnesia. Since the use of muffle furnaces has been discontinued in the year 1892, no more of this *stupp fett* has been produced. For treatment in shaft furnaces at Idria, the soot from the condensing chambers of the flues, together with the residues of the furnace soot, were mixed with ground clay, pressed, and moulded into lumps, which were treated together with poor coarse ore. The coal used was mixed with a certain quantity of coke. Further quantities of residues were treated in the Czermak furnaces and in the reverberatory furnaces, together with the ores suitable for treatment in these furnaces. In California the residues are worked either by themselves in retorts or together with the ores in the furnaces suitable to the various grades. In New Almaden, in the year 1888, 18 per cent. of the total mercury production was obtained from soot. Recently at Idria, of the total production of mercury, including a loss of 9 per cent., 56 per cent. was obtained by pressing the soot and 15 per cent. by distillation of the soot residues.

The acid water from the condensers contains sulphuric and sulphurous acids, sulphates of iron, mercury, calcium and ammonia, hydrocarbons, and in some cases small quantities of hydrochloric acid and floured mercury. According to Janda,[1] the acid water condensed in the year 1892 at Idria in the condenser of shaft furnace No. X. had the following composition:—

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[1] Mitter, *loc. cit.*

	Per cent.
Hg_2O	0·33
FeO	14·38
CaO	0·50
SO_3	11·01
SO_2	1·97
NH_3	0·61
HCl	0·06
Condensible hydrocarbons, including the acetic acid series	22·12
Water and undetermined	48·12

The specific gravity of this water was 1·65 at 15° C. If the acid water contains floured mercury, as is, for instance, the case at New Almaden, it is freed from it by filtration through charcoal. The water runs off clear, leaving a black slime upon the filter. The latter is dried and is then distilled, together with the ores.

Distillation Residues. When the operation is carried on properly, the residues are so poor in mercury that they can be thrown away. For example, the residues from the Idrian shaft furnaces contained in 1877[2] 0·002 per cent. of mercury, and those from the reverberatory furnaces[3] contained 0·006 per cent. in 1877, 0·0001 per cent. in 1879, and in 1892 only traces of mercury.

The General Arrangement of a Mercury Works

As an example of the general arrangement of a quicksilver works with modern furnaces, condensers and fan, the plant at Idria may be described. The ores there average upon the whole 0·5 to 0·8 per cent. of mercury. The ores were formerly divided into slimes, fine ore, coarser ore and lump ore, but now the 4 following divisions are made:—

1. *Reicher Erzgries.*—"Rich small ore" with about 6 per cent. of mercury. This is divided into 2 classes: (1) of 0·16 to 0·32 inch mesh, and (2) below 0·16 inch. Both grades are again subdivided into those containing more than 10 per cent. and those containing less than 10 per cent. of mercury.

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[1] *Oesterr. Zeitschr.*, 1894, p. 270.

[2] *Idrianer Festschrift.*

[3] *Idrianer Festschrift.*

2. *Armer Erzgries prima.*—'Poor small ore of first quality," containing 0·7 per cent. of mercury and less than 0·8 inch in size.

3. *Armer Erzgries secunda.*—" Poor small ore of second quality,' containing 0·4 per cent. of mercury and 0·8 to 1·2 inch in size.

4. *Arme Erzgröb.*—" Poor coarse ore," containing 0·3 per cent. of mercury, and 1·2 to 4 inches in size.

The complete analyses of the various grades of ore were as follows in the year 1881:—[1]

	Slimes.	Fine Ore	Coarse Ore
	Per cent.	Per cent	Per cent.
Mercuric sulphide	0·62	1·25	8·56
Mercurous chloride	trace	trace	0·22
Basic mercuric sulphate .	—	—	trace
Ferrous carbonate . .	0·76	3·17	4·27
Calcic carbonate	35·75	27·21	14·71
Calcic sulphate	0·53	1·46	2·42
Magnesic carbonate . .	27·17	20·33	4·20
Magnesic sulphate	0·21	0·55	1·11
Iron bi-sulphide . .	4·24	4·31	5·09
Alumina	1·64	1·61	1·30
Phosphoric acid . . .	—	—	trace
Aluminic silicate . .	16·48	22·75	15·82
Ferrous silicate .	—	trace	20·18
Silica . . .	11·52	16·48	17·64
Bitumen	1·08	1·63	3·97
Water and loss . . .	—	—	0·49

The composition in 1892[2] was the following:—

	Rich Small Ore.	Poor Small Ore.	Poor Coarse Ore.
	Per cent.	Per cent.	Per cent
HgS	6·74	0·95	0·38
FeS_2 . . .	9·49	11·64	4·45
$FeCO_3$ . .	2·52	6·66	4·76
$CaCO_3$	26·18	27·13	34·86
$MgCO_3$ . . .	16·69	10·24	24·92
$CaSO_4$	1·05	2·93	0·79
$MgSO_4$	0·44	0·74	0·32
$Ca_3P_2O_5$	0·75	0·41	0·32
Al_2O_3 (amorphous)	2·60	4·80	3·53
SiO_2	30·04	31·77	28·82
Bitumen	0·97	0·70	0·68
Organic matter and water of crystallisation	2·53	2·03	1·17
Cl	distinct trace	—	—

The ores are treated by heating them with access of air in the furnaces already described. The rich small ore is treated in the Czermak furnace, the poor small ore of first quality in Czermak furnaces and long-bedded calciners, the poor small ore of second quality and the poor coarse ore in shaft furnaces. The works contain 3 Czermak furnaces, 8 long-bedded calciners, and 9 shaft furnaces. The practical results obtained, which have already been set forth under the heads of the various individual furnaces, together with the annual mercury production of the furnaces, is shown in the following table of the results obtained in the year 1892:—

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[1] *Idrianer Festschrift*, Vienna, 1881. [2] Janda, *Oesterr. Zeitschr.*, 1894, p. 267.

Class of Furnace.	Grades of material treated.	Amount treated per day per furnace	Wages.		Fuel consumption per 10 tons of ore.	Soot production.	Mercury production.
			per 10 tons of ore.	per 100 kilos (2 cwt.) of mercury.			
		Tons.	s. d.	s. d.	cubic feet.	%	Tons.
Novak shaft furnaces	Poor coarse ore and soot	12·15	13 4	42 1	58·3 charcoal	0·5	109·915
Czermak furnace, No. 1	Poor and rich small ore and soot . .	22·46	17 9	5 10	130·7 wood	3·3	204·272
Czermak furnaces, Nos. 2 and 3	Poor small ore and soot	26·75	14 0	19 1	106·6 ,,	1·3	117·754
Calciners, Nos. 1 to 6	Poor small ore and soot . . .	6·6	21 6	29 9	148·9 ,,	1·9	71·257
Calciners, Nos. 7 and 8	Residues from old Leopoldi furnaces and soot .	6·85	23 10	119 5	156·5 ,,	2·0	8·659

The temperature at which the gases and vapours escape from the various furnaces[1] are, upon the average:—

Long-bedded calciners	341° C.
Czermak furnaces	353° C.
Shaft furnaces	226° to 233° C.

In Fig. 272 a general ground plan of the works is given, showing the connection of the furnaces with the condensers, the mode of communication of the various condensers with the underground central condensing chambers and the connection of the latter with the fans. The draught was first produced by a stack alone and then by means of a furnace connected with the stack, but recently fans have been employed for this purpose. They are found to have an especially good effect upon the general mode of working, the health of the men engaged, and the diminution of the losses of mercury. There are two fans, one of which is in reserve. The fans were first made of cast iron, then of varnished sheet iron, and finally of sheet brass. All these materials have, however, at present been replaced by others, the disc of the fan now consisting of brass, whilst the vanes are made of sheet copper; the diameter of the fan is 8 feet and its

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[1] Janda, *Oesterr. Zeitschr.*, 1894, p. 298.

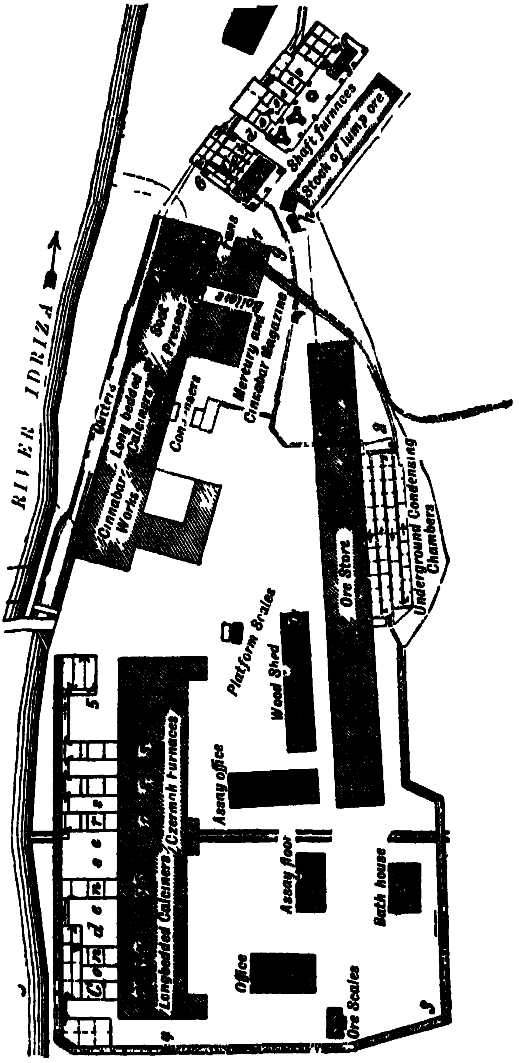

FIG 272.

speed is between 180 and 280 revolutions per minute, producing a normal depression of 0·7 inch water gauge. The cubical contents of the various condensers and flues is shown in the following table:—

	Volume of Condensers.		
	Chambers.	Flues.	Total
	cubic feet.	cubic feet.	cubic feet.
Shaft furnaces . .	33,568	6,569	40,137
Czermak furnaces .	35,916	2,013	37,929
Calciners 1 to 6 . . .	50,148	706	50,854
Calciners 7 and 8	3,885	742	4,627

To these must be added the space common to all the furnaces, viz.:—

	Chambers.	Flues.	Total.
	cubic feet.	cubic feet.	cubic feet.
Underground central chambers .	63,285	—	63,285
Flues connecting the calciners and Czermak furnaces above ground .	-	20,236	20,236
Flue from the central chamber to the fan	—	4,944	4,944
Flue from the fan to the stack . .	-	18,576	18,576

The total contents of the condensing appliances therefore amount to:—

Chambers	186,802 cubic feet
Flues	53,786 „ „
Total	240,588 „ „

The gases and vapours from the shaft furnaces enter the condenser at a temperature of 114° C., and leave it at 15° C.; those from the Czermak furnaces enter with a temperature of 109° to 180° C., and escape at 21° to 30° C.; those from the calciners enter at 174° C. and escape at 25° C. According to Mitter, the average of the mercury extracted in the years 1890 to 1892 was obtained:—

	Per cent.
From the condensers and from pressing the soot. .	74·64
From the residues of the soot	14·89
From the soot collected in the more remote flues and chambers	5·22
Loss of mercury	8·25

According to recent communications from Mitter in Idria the extraction of mercury is at present distributed as follows:—

	Per cent
No. 1. Metallic mercury taken direct from the condensers	20
No. 2. Obtained by pressing the soot	56
No. 3. Obtained by treatment of the soot residues (about)	15
Loss of mercury „	9

Nikitowka, Russia [1]

These works were started on a working scale in 1886 to treat cinnabar ores from the Carboniferous formation. These ores contain on the average 0·6 per cent. of mercury. They are broken in rock breakers and dropped on to a picking belt, on which about 16 per cent. of barren rock is picked out. Lump ores in sizes up to that of twice a man's fist are treated in barrel-shaped furnaces of 16 feet 6 inches in height and 11 feet 6 inches in diameter in the widest part, the ore being mixed with coal. The condensing appliances consist of Y-shaped pipes made of cast iron lined with cement. The small ore and the dust from the dressing works, which is rich in mercury, together with the soot residues, are treated in furnaces similar to the already described Idrian Czermak furnaces, 4 of which form one block. The condensers are similar to those already described. The soot is treated in rotating barrels with lime, whereby the greater portion of its mercury is extracted. The output of mercury from the ores is given as 0·563 per cent., the loss of mercury during treatment at 12 per cent. The output of mercury in the year 1891 amounted to 291¼ tons.[2]

THE EXTRACTION OF MERCURY FROM MERCURIAL FAHLORES

Mercury is obtained as a bye-product during the calcination of mercurial fahlores. The author has seen mercury obtained in this way at the Stefan Works, near Göllntz, in Upper Hungary. Antimonial fahlore, containing 30 to 39 per cent. of copper, 25 to 33 per cent. of antimony, 0·10 to 0·12 per cent. of silver, and 0·52 to 17 per cent. of mercury, with an average content of 1·63 per cent. of mercury, is there treated in circular stalls, 23 feet in diameter and 6 feet

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[1] *Russian Mining Journal* (*Gorni Journal*), 1891, No. 20.

[2] Ernst, *Die mineralischen Bodenschätze des Donetz-Gebietes*, Hanover, 1893.

6 inches high, which are covered over. These stalls, the lower portion of which is provided with draught-holes for the admission of air, contain 67 to 70 tons of ore. The ores are piled upon a bed of cord-wood; layers of wood are also introduced between the ores in such a way that spaces are produced, which become filled with charcoal, and, after the latter is burned, serve as air flues. During the calcination of the ore, the mercury is evolved in the metallic state and is condensed in the topmost layers of ore. When the latter, in the course of continued calcination, get heated, fresh ore is piled on, into which the mercury is then driven, and where it condenses. After the completion of the calcination, which lasts 3 to 4 weeks, the upper layers of ore are taken off and washed in tyes for the extraction of the mercury. The mercury obtained is distilled in iron retorts and then packed in sheepskin bags. The residues from washing and from distillation are treated for copper and silver. With such a process the loss of mercury by the escape of mercury into the air, the sides and the floor of the stalls is unavoidable

EXTRACTION OF MERCURY FROM METALLURGICAL PRODUCTS

The chief metallurgical products containing mercury are soot and the amalgams obtained in the course of gold and silver extraction. The process of soot treatment has already been described. The extraction of mercury from gold and silver amalgams when these metals are obtained by amalgamation, has been fully considered in Volume I., pages 703 and 802. Mercury is also obtained in small quantities from the flue-dust resulting from the calcination of blende rich in mercury, as also from the slimes of the lead chambers, in which the sulphur dioxide evolved on calcining these blendes is converted into sulphuric acid. The Swedish blende calcined at Oberhausen contains 0·2 per cent. of mercury according to Bellingrodt.[1] The flue-dust which is deposited during the calcination in the dust chambers nearest the calcining furnace contains 67 per cent. of mercury, the slimes of the lead chambers into which the products of calcination are conducted 4 per cent. of mercury. Both these bye-products are treated for the mercury they contain. The mode of treatment is not mentioned, but it is probably by distillation.

THE EXTRACTION OF MERCURY IN THE WET WAY

The extraction of mercury in the wet way has been repeatedly proposed, but has not yet been introduced, nor is there any prospect of its introduction. Sieveking[1] proposes to treat ores containing cinnabar with a solution of cuprous chloride in salt in the presence of a granulated alloy of copper and zinc in revolving barrels. Cinnabar is thereby decomposed with the liberation of mercury and the formation of cupric sulphide and cupric chloride, as shown by the equation:—

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[1] *Chem. Ztg.*, 1886, No. 68.

$$Cu_2Cl_2 + HgS = CuCl_2 + CuS + Hg.$$

Metallic mercury amalgamates with the copper-zinc alloy, and can be removed from the latter by distillation. This process does not seem to have been satisfactory the use of cupric chloride was found to be equally unsatisfactory Alkaline sulphides containing caustic alkalies (see page 253) also gave unfavourable results. Solutions of bromine in water and of bromine in concentrated hydrochloric acid, which had been proposed by R. Wagner,[2] have not come into use. Mercury can be extracted from substances containing mercurous chloride by solutions of hyposulphites.

The Electrolytic Extraction of Mercury

No attempts have yet been made to extract mercury electrolytically. In view of the simplicity of the other methods of mercury extraction, it is doubtful whether the electrolytic method, admitting even its possibility in the case of poor ores, would prove more advantageous than the dry method, in spite of the losses in the latter. It must, however, be admitted that cinnabar is readily soluble in solutions of alkaline sulphides containing caustic alkalies, and that the electrolysis of the solutions of mercury sulphide and oxide thus obtained should offer no difficulties, and would not require any very high electric tension.

According to Brand,[3] cinnabar is said to be readily decomposed at the anode of an electric circuit, whilst mercury is thrown down at the cathode, a solution of common salt or dilute hydrochloric acid being employed as a bath. The tension in the bath is said to amount to 1 volt. The power to extract 1 kilogramme of mercury in this way would accordingly amount to

$$\frac{1 \text{ volt} \times 266{\cdot}5 \text{ ampères}}{650 \text{ Watts} \times 0{\cdot}75} = 0{\cdot}54 \text{ horse-power per hour,}$$

since 266·5 ampères can deposit 1 kilogramme of mercury per hour, and since one horse-power, assuming 12 per cent. of loss in conversion, would yield not 735, but 650 Watts, and since the loss of current by conversion into heat, by short-circuiting, &c., amounts to 25 per cent. As 2 kilogrammes of coal would be required per horse-power per hour, the coal consumption per kilogramme of mercury would come out at 1·08 kilogrammes. With the most modern steam engines, the loss of power in the conversion of mechanical work into electrical energy amounts to 9 per cent., and in the dynamo to 6 per cent., making a total of 15 per cent., whilst the loss of current in the conductors may be taken as 10 per cent., and the consumption of coal in the best steam engines amounts to 1 to 1·5 kilogrammes per horse-power per hour. Under these circumstances the extraction of mercury in the above manner would seem to be not altogether without hopeful possibilities.

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[1] *Oesterr. Zeitschr.*, 1876, No. 2; *Berg. und Hutt. Ztg.*, 1876, p. 169.

[2] *Dingler*, vol. 218, p. 254; *Chem. Centralblatt*, 1878, p. 711.

[3] Dammer, *Chem. Technologie*, vol. ii., p. 41.

THE MANUFACTURE OF ARTIFICIAL CINNABAR

At many works a portion of the mercury extracted is converted into artificial cinnabar, as, for instance, [redacted] in Carniola. A short account of the preparation of cinnabar at this place, as far as it is not kept secret, will accordingly be given. Artificial cinnabar can be produced both in the dry and wet way. In the dry way the sulphur is combined directly with mercury. For the production of cinnabar in the wet way metallic mercury or compounds of mercury, together with sulphur, are treated with solutions of caustic soda or potash, with potassic or sodic polysulphides, with ammonic sulphide or with sodic hyposulphite at suitable temperatures. Processes for the production of cinnabar in the wet way have, for example, been devised by Kirchhoff, Brunner, Firmenich, Liebig, Martens, Fleck, Gautier-Bouchard, Hansamann, and Jean Maire. At Idria cinnabar has been produced in the dry way for a long time. Since 1880 it has also been manufactured in the wet way successfully*; nothing, however, can be said about the latter process, as it is kept secret.

Cinnabar is produced in the dry way at Idria by mixing together mercury and sulphur in revolving barrels, heating the mixture produced in iron retorts so as to complete the combination of sulphur with mercury, volatilising the excess of sulphur, and finally subliming the cinnabar thus formed, which is then ground and refined by being boiled with a solution of potash. The first operation, or the mixing of sulphur and mercury, is known as amalgamation or the preparation of the *moor*. The second operation, or heating the mixture in retorts, is known as subliming the *moor*, or the production of lump cinnabar. The third operation, grinding the lump cinnabar; and the last, the refining of cinnabar. The first operation consists in mixing pounded sulphur which is passed through a sieve of ¾ inch mesh, with mercury in small horizontal rotating casks made of elm, with internal projecting ridges. 16 parts of sulphur are added to 84 parts of mercury; the charge for a barrel amounts to 55 lbs. The barrels make 60 revolutions per minute, 30 to the right and 30 to the left. After 2 or 3 hours' treatment, the black mass thus produced, known as the crude *moor*, is removed from the barrels and submitted to the second operation. The second operation, or sublimation, is performed in cast-iron or pear-shaped retorts, each of which holds 114 lbs. of *moor*. There are six of these retorts in a reverberatory furnace heated with wood. Three stages are distinguished in this operation, viz. *abdamfen* ("boiling off"), *stücken* ("forming lumps"), and *sublimiren* ("sublimation"). In the first stage the combination of sulphur and mercury is completed; the retorts are covered with hoods of sheet iron, the necks of which point upwards and project from the arch of the furnace. The heat is raised slowly, and in fifteen minutes after firing has commenced the combination of sulphur and mercury is effected with a violent detonation, whilst a flame is projected from the retort. At the commencement of the second stage, which now follows, the sheet-iron hoods are replaced by hoods of clay, and the fire is gradually raised for 2½ hours, during which time the excess of sulphur is volatilised. At the commencement of the third stage, condensers are attached to the hoods, which are also made of clay, and the fire is raised until the cinnabar sublimes. That known as lump cinnabar deposits first in the cooler portions of the condensers and afterwards in the hoods, this sublimation lasting about 4 hours. It is complete when flames of burning sulphur are visible from time to time about the hood and condenser. The latter are now removed, and after the greater portion of the cinnabar has been extracted from them they are broken into pieces and the fragments are carefully cleaned from any cinnabar that may adhere to them. Lump cinnabar and scrapings are thus obtained, the latter being added during the next sublimation. Of the lump cinnabar 70 per cent. is obtained from the hoods, 25 per cent. from the first, and 5 per cent. from the second condenser. The lump cinnabar is ground under water to prevent any loss of dust, and to obtain it in the form of as uniform a powder as possible. The mill consists of a fixed stone and a horizontal stone runner, the latter revolving in a wooden casing at the rate of 40 revolutions per minute. The ground cinnabar, known as vermilion, flows from a spout into a clay vessel placed beneath it. If a lighter shade of cinnabar is required, it must be ground repeatedly, up to five times. At each fresh grinding the distance between the grindstones is decreased. Three grades of vermilion are made, viz., bright red, dark, and Chinese vermilion. To improve its colour, vermilion is subjected to what is known as refining. This consists in boiling the vermilion with a solution of potash of 10° to 13° B. in cast-iron kettles. The charge for each consists of 2 cwt. of vermilion and 48 to 50 lbs. of lye. The boiling lasts for ten minutes. At the end of this time the vermilion is allowed to settle, and it is then ladled into tanks. The lye that is left in the kettle is used to treat two charges more. The vermilion is repeatedly washed with hot water in the tanks, and then freed from excessive water by filtering through canvas. It is finally dried in clay pans at a temperature of 62° to 88° C. The dry vermilion is crushed under wooden hand-rolls, and is then sent into the market packed in sheepskins or in bags. The production of cinnabar in the wet way, as already mentioned is kept secret.

BISMUTH

PHYSICAL PROPERTIES

BISMUTH has a characteristic reddish-white colour and high lustre. It crystallises in the hexagonal system in obtuse rhombohedra with an angle of 87° 40′, which have the appearance of cubes. Its fracture is coarsely crystalline. Its hardness is low, between 2 and 2·5, and it is so brittle that it can be pounded. Molten bismuth expands on solidifying by 2·35 per cent. According to Roberts, the specific gravity of solid bismuth is 9·82, of fluid bismuth 10·055. The melting point of bismuth is given by Rudberg and Riemsdijk as 268·3° C.; by Person as 270·5° C. Ledebur found that commercial bismuth melts at 260° C. According to Classen pure bismuth produced by electrolysis melts at 264° C. At a high temperature molten bismuth volatilises; its boiling point has not been exactly determined, but according to Carnelly it lies between 1,090° and 1,450° C. Bismuth has the lowest thermal conductivity of any of the metals; it amounts to 18 compared to that of silver taken as 1,000. Regnault gives the specific heat of bismuth between 0° and 100° C. as 0·0308. The linear expansion of bismuth by heat between 0° and 100° C. amounts to $0{\cdot}001341 = \frac{1}{746}$ of its length at 0° C., according to Calvert and Johnson. The electric conductivity of bismuth is 1·19 at 13·8° C. according to Matthiesen, that of silver at 0° being taken as 100. Bismuth is the most strongly diamagnetic of all bodies.

Commercial bismuth is generally rendered impure by an admixture of foreign bodies, chiefly silver, lead, copper, arsenic, iron, nickel, cobalt and sulphur, at times also thallium and tellurium, which affect the above-named physical characteristics. When impure bismuth is melted and allowed to solidify, in the act of solidification numerous globules of pure bismuth, or in the case of the presence of lead and silver, of bismuth alloyed with these metals, are extruded. Pure bismuth does not show this phenomenon. It depends upon the fact that the alloys of bismuth with bodies other than lead and silver expand on solidification, and therefore expel the bismuth, or the alloys of bismuth with lead and silver, which will still be fluid, on account of their low melting point. This phenomenon must be borne in mind in taking samples of bismuth.

THE CHEMICAL PROPERTIES OF BISMUTH AND ITS COMPOUNDS THAT ARE OF IMPORTANCE IN ITS EXTRACTION

Bismuth is not affected in the air at ordinary temperatures. Heated in the air, it is covered shortly before melting with a grayish-black coating of bismuthous oxide; if the heating is continued up to redness, a film of bismuthic oxide forms, which is yellow or green in the case of pure bismuth, but has a violet or blue colour if the metal is impure. At bright redness it burns with a bluish flame to bismuthic oxide, which appears in the form of a yellow smoke. Water free from air does not affect bismuth at ordinary temperatures; when containing air it affects it slowly, converting it into a basic carbonate. Water vapour is decomposed by bismuth only at a white heat, and then but slowly. Bismuth combines directly with chlorine, bromine and iodine. Nitric acid and aqua regia dissolve bismuth readily. Dilute sulphuric acid and cold sulphuric acid do not attack it; it is, however, dissolved by hot concentrated sulphuric acid with the formation of bismuthic sulphate and the evolution of sulphur dioxide. Dilute hydrochloric acid does not attack it; hot concentrated acid dissolves it, but with difficulty. Bismuth is precipitated as metal from solutions of its salts by metals of the alkalies and the alkaline earths, zinc, manganese, iron, nickel, cadmium, copper, tin and lead.

Oxides of Bismuth

Bismuth forms four compounds with oxygen, viz., bismuthous oxide (Bi_2O_2), bismuthic oxide (Bi_2O_3), bismuth tetroxide (Bi_2O_4), and bismuthic anhydride (Bi_2O_5). Bismuthous oxide (Bi_2O_2) is obtained in the form of a brown precipitate when a mixture of solutions of bismuthic and stannous chlorides is poured into dilute solution of caustic potash. When dried and heated in the air it burns to bismuthic oxide. Bismuthous oxide is produced in the dry way as a grayish black powder when metallic bismuth is heated in the air to near its melting point. In moist air it becomes more highly oxidised, and when heated in the air is transformed into yellow bismuthic oxide. Bismuthic oxide is obtained by oxidising the metal at a red heat, by heating bismuthic nitrate or carbonate, as also by precipitating bismuthic hydrate from a solution of the nitrate by a solution of potash or soda, and heating the solution to boiling. Bismuthic oxide is a yellow powder soluble in nitric, hydrochloric and sulphuric acids. It melts at a red heat to a reddish brown fluid, which solidifies to a yellow crystalline mass. Bismuthic oxide shares this property of fusibility with lead oxide. Bismuth can therefore be cupelled off from silver in the same way as lead. As, however, bismuth is more difficultly oxidisable than lead, the lead may be partly cupelled off from bismuth; on the other hand, bismuthic oxide is much more readily reduced to metal than lead oxide, so that molten bismuthic oxide is reduced to the metallic state by lead. Bismuthic oxide is reduced to bismuth on a large scale by means of carbon. This oxide shows in its chemical affinities great similarity with the corresponding oxide of antimony. It has but little affinity for acids; its salts are decomposed by the addition of a large volume of water, with the formation of basic salts. Bismuth tetroxide (Bi_2O_4) corresponds with antimony tetroxide, and may be looked upon as bismuthic bismuthate ($BiOBiO_3$). It is obtained by melting bismuthic oxide with caustic potash in the air, by igniting bismuthic oxide, caustic potash and chlorate of potash in a silver crucible, as also by treating bismuthic oxide suspended in water with caustic potash and chlorine until the mass assumes a yellowish red colour. If chlorine is passed for a further period into the solution, compounds of the alkaline bismuthate with bismuthic acid form. By digestion in dilute nitric acid and washing, bismuthic acid ($HBiO_3$) can be separated. Bismuthic anhydride (Bi_2O_5) is obtained by heating bismuthic acid to 130° C. If heated still further, bismuthic anhydride evolves oxygen. It is also decomposed by sulphuric acid and hydrochloric acid, with the evolution of oxygen or chlorine.

Chlorides of Bismuth

Bismuth forms two compounds with chlorine, viz., bismuthous chloride (Bi_2Cl_4) and bismuthic chloride ($BiCl_3$). Bismuthous chloride is obtained by heating pulverised bismuth with mercurous chloride, or by melting bismuthic chloride and bismuth together. It forms a black substance which attracts moisture from the air, and is decomposed by water and by dilute mineral acids. When heated more strongly, it is decomposed into volatile bismuthic chloride and bismuth.

Bismuthic chloride ($BiCl_3$) is obtained by heating bismuth in chlorine gas, by heating pulverised bismuth with mercuric chloride, and by dissolving bismuthic oxide in hydrochloric acid. It forms a white mass, deliquescent in air, which is volatile at 427° to 439° C. It is decomposed by water, and if a sufficient quantity of water is employed, the whole of the bismuth present is precipitated as oxychloride in accordance with the equation :—

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

The oxychloride forms a dazzling white powder, which was formerly used as a cosmetic.

Oxy-Salts of Bismuth

Of the oxy-salts of bismuth, the sulphate and nitrate are the most important. There are several compounds of bismuth with sulphuric acid which can be produced by dissolving bismuthic oxide in sulphuric acid. From some of these compounds water precipitates basic bismuthic sulphate. Bismuthic sulphate is decomposed on heating, although imperfectly, into the oxide and sulphur trioxide, or sulphur dioxide and oxygen. Bismuthic nitrate $Bi(NO_3)_3$ is obtained by dissolving bismuth in nitric acid. It forms colourless crystals with 5 molecules of waters of crystallisation. Water precipitates a basic nitrate from the solution, whilst acid salts remain dissolved. Basic bismuth nitrate is used in medicine and as a cosmetic.

Sulphides of Bismuth

Bismuth forms two compounds with sulphur, viz., bismuthous sulphide (Bi_2S_2) and bismuthic sulphide (Bi_2S_3). Bismuthous sulphide (Bi_2S_2) is obtained in combination with water on treating the solution of a bismuthous salt with sulphuretted hydrogen in the absence of air. A black powder of the composition $Bi_2S_2 + 2H_2O$ is thus obtained. In the dry way bismuthous sulphide is produced by melting together sulphur and bismuth in the proportion of their atomic weights. At a strong heat it is decomposed into bismuthous sulphide and metallic bismuth. Bismuthic sulphide (Bi_2S_3), which is found in nature as bismuth glance, can be obtained in the form of a bluish gray foliated mass by melting bismuth with an excess of sulphur; in the wet way it is produced in the form of a blackish-brown precipitate by passing sulphuretted hydrogen into a solution of bismuthic salts. It is soluble in boiling concentrated hydrochloric acid and in nitric acid. If water vapour is passed over red-hot bismuthic sulphide, according to Regnault, sulphuretted hydrogen, bismuthic oxide, and a small quantity of metallic bismuth are produced. By passing hydrogen over red-hot bismuthic sulphide, sulphuretted hydrogen and metallic bismuth are obtained. Bismuthic sulphide heated in the air is converted into bismuthic oxide and bismuthic sulphate, sulphur dioxide being evolved. The sulphate is only imperfectly decomposed by increasing the temperature. A mixture of bismuthic oxide and sulphate are therefore always obtained as the products of the oxidising roasting of bismuthic sulphide. Bismuthic sulphide can be melted with metallic bismuth in all proportions. It is said that at very high temperatures the sulphur can be volatilised almost completely.

The compounds of bismuth with phosphorus and arsenic are decomposed on heating. Bismuth phosphide is completely decomposed into phosphorus and bismuth. The last portions of arsenic can, however, only be removed with difficulty from arsenide of bismuth.

Alloys of Bismuth

Bismuth alloys with a number of metals, and causes the resulting alloys to melt at a low temperature. Alloys which are used in the arts on account of their low melting points are those of Newton, Rose, Lichtenberg. Wood and Lipowitz. Their compositions and melting points are shown in the following table:—

Alloy of	Composition.				Melting Point
	Bi	Pb	Sn	Cd	
Newton	2	5	3	—	94·5° C.
Rose	2	1	1	—	93·75°
Lichtenberg . . .	5	3	2	—	91·6°
Wood	4	2	1	1	71·0°
Lipowitz . . .	15	8	4	3	60·0°

These are used for light solders, for stopping teeth, for taking impressions of woodcuts and coins, and for safety-plugs for boilers.

Zinc will only take up 2·4 per cent. of bismuth, whilst bismuth will take up as much as 14·3 per cent. of zinc. Antimony alloys with bismuth in all proportions. If an alloy of lead and bismuth is heated in the air to redness, the lead oxidises first, and, after its removal, the bismuth. On account of the easy fusibility of lead oxide, it is therefore possible to separate lead from bismuth by an oxidising fusion of the alloy. When such an alloy is treated by the Pattinson process,[1] the bismuth may be collected in an alloy rich in bismuth, whilst the bulk of the lead is obtained free from bismuth,[2] the bismuth following the silver into the enriched lead. If an alloy of lead and bismuth with silver or gold is heated in the air, the lead is first oxidised, and then the bismuth, the silver or gold retaining a small proportion of the bismuth.

From alloys of gold and bismuth containing but small quantities of gold, the gold may be removed by means of zinc, a small portion of the bismuth being, however, retained in the zinc and gold alloy.[3]

Ores of Bismuth

The ore which furnishes the greatest quantity of bismuth is metallic bismuth. It is found in Europe in the Erzgebirge of Saxony (Schneeberg, Johann-Georgenstadt, Schwarzenberg, Altenberg, Zinnwald); in Bohemia (Joachimsthal), Carinthia (Lölling), Styria (Salzburg), the Banate (Cziklova); Sweden (Fahlun); Norway (Bleka); England (Redruth, Cornwall, and Carrick Fell, Cumberland); Scotland (Alva, Stirlingshire). Outside of Europe it occurs in the United States of North America (Utah), in Peru, Chili (San Antonio del Potrero Grande), and more particularly in Bolivia (Illimani, Tasna, Chorolque, Oruro, Guaina, Potosi, Sorata), and in Australia (Queensland and New South Wales).

Bismuth ochre (Bi_2O_3), containing 89·7 per cent. of bismuth, and generally intermixed with iron, copper and arsenic, occurs in Bohemia, Siberia, Cornwall (St. Agnes), France (Meymac, Dep. Corrèze), and in Bolivia. This mineral is often mixed with bismuthic carbonate and hydrate. Bismuthic carbonate or hydrocarbonate occurs by itself in Cornwall, France (Meymac), Bolivia, United States of North America (Arizona), and Australia (Queensland).

Bismuth glance or bismuthine (Bi_2S_3), containing 81·25 per cent. of bismuth, occurs in Cumberland, Cornwall, Saxony, Sweden, Bolivia, Colorado and Queensland. The other minerals containing bismuth are of no importance for the extraction of that metal. Among these may be enumerated copper bismuth glance (wittichenite), silver bismuth glance, bismuthic cobaltic pyrites, bismuthic nickel pyrites, bismuthic silicate (eulytine), telluride of bismuth (tetradymite), seleno- and sulpho-telluride of bismuth and needleore (aikinite).

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[1] Vol. i , p. 503.

[2] Matthey, *Proc. Royal Society*, vol. xiii., p. 89.

[3] Matthey, *loc. cit.*

Furnace Products containing Bismuth

The bismuth which occurs in small quantity in various ores is concentrated in certain metallurgical products, the latter of which, therefore, form the material for the extraction of bismuth; among such metallurgical products may be mentioned work-lead, litharge, hearths, cupel bottoms, nickel and cobalt speiss.

EXTRACTION OF BISMUTH

Bismuth is extracted both in the dry way and by means of the wet way. The electrolytic method of bismuth extraction has been proposed for alloys of bismuth and lead, but has not as yet been adopted to any extent. By far the greatest portion of the bismuth that is at present produced, is got in the dry way at the cobalt works at Oberschlemma and Pfannenstiel in Saxony, which treat principally ores from Schn[illegible]berg and Austro-Hungary, and from the works of Johnson, Matthey and Co., in London, which treat chiefly Australian and South American ores.

The dry method should be used as a rule for ores rich in bismuth and for ores containing bismuth in the metallic state. The wet way is employed for the extraction of bismuth from a series of metallurgical products, from poor oxidised bismuthic ores, as also for the extraction or removal of bismuth from the ores which contain it as a subsidiary constituent (tin ores carrying bismuth). Bismuth obtained in the dry or wet way is generally rendered impure by a number of foreign bodies which interfere with its employment for certain purposes, especially for the preparation of pharmaceutical products. It has, therefore, to be refined.

EXTRACTION OF BISMUTH IN THE DRY WAY

The extraction of bismuth in the dry way from ores varies with the composition of the latter, and depends upon the low melting point of the metal, the decomposability of the sulphide by iron, and the possibility of converting bismuthic sulphide into a mixture of sulphate and oxide by means of an oxidising roasting, and the reducibility of the oxide by means of carbon, and upon the difficulty of oxidising bismuth in the air at high temperatures. On account of the low melting point of bismuth, it can be separated by simple fusion from the minerals and gangue accompanying it. The fusion may take the form either of a liquation of the bismuth from the accompanying minerals, or of a fusion of the bismuth and accompanying minerals with the formation of a slag. Bismuth is extracted from bismuthic oxide by a reducing fusion with carbon, the other constituents being slagged off. From bismuthic sulphide, bismuth can be obtained either by an oxidising roasting followed by a reducing fusion with carbon, or by melting with iron with the formation of ferrous sulphide and separation of bismuth. From its alloys with lead, bismuth may be extracted by cupellation of the latter until the lead has been removed in the form of litharge. From alloys of the precious metals bismuth may be extracted by cupellation, and reduction of the bismuthic oxide thus obtained by means of carbon. We have accordingly to distinguish:—

(1) The extraction of bismuth from ores.
(2) The extraction of bismuth from metallurgical products.

i. THE EXTRACTION OF BISMUTH IN THE DRY WAY FROM ORES

Under this heading we have to distinguish:—

(*a*) The extraction of bismuth from ores containing it in the native state.

(*b*) The extraction of bismuth from bismuthite.

(*c*) The extraction of bismuth from ores which contain it in an oxidised state.

a. The Extraction of Bismuth from Ores containing the Native Metal

Bismuth may be separated from ores containing it in the form of metal, either by a process of liquation or by fusion, in which the entire mass is liquefied. The objection to the process of liquation is that the bismuth is only imperfectly extracted by it, and that other compounds of bismuth, which frequently occur intermixed with the native metal, are not extracted, and remain in the residues. Fusion processes proper, on the other hand, not only yield, on account of the liquefaction of the entire mass, a much better output of native bismuth, but also admit of the addition of desulphurising or reducing agents to the ores, which will simultaneously extract the bismuth from the sulphur or oxygen compounds that may be contained in the ores, together with the native bismuth. The extraction of bismuth by the fusion process is, therefore, preferable to employing liquation; for which reason the latter process, which was formerly employed, has now been replaced everywhere by the former methods.

The Extraction of Bismuth by Liquation

This process was formerly in use in Saxony. It was carried out in inclined cast-iron pipes, from the lower end of which the bismuth flowed out as soon as it had reached its melting point, whilst the difficultly fusible gangue remained behind. The older liquation furnaces were designed by Plattner, and have been afterwards suitably modified by Günther. Plattner's furnace is shown in Fig. 273, in which *r* is the grate, *E* the furnace body, *f*, *f* are stacks, *s*, *s* are the inclined cast-iron pipes, which—eleven in number—are arranged in two tiers. They are 4 feet long, 10 to 12 inches high and 6 to 8 inches broad, each holding up to 33 lbs. of ore. They are charged from the upper end, which, during the course of the operation, is kept closed by a sheet-iron cover. The liquid bismuth flows out from the pipes through a small opening, *o*, at their lower ends, into two gutters *a*, inclined towards the centre of the furnace, which discharge into a movable kettle *b*, which is kept heated. Moulds supported upon a carriage are run underneath the lip of the kettle, and the fluid bismuth collected in the latter is poured into them. The residues from the liquation are drawn out at the upper end of the pipes and fall into a box provided with a perforated bottom and standing in water, which can be lifted out from the tank in which it rests. By dropping these residues into water they are at once cooled, and there is nothing to prevent the pipes being immediately

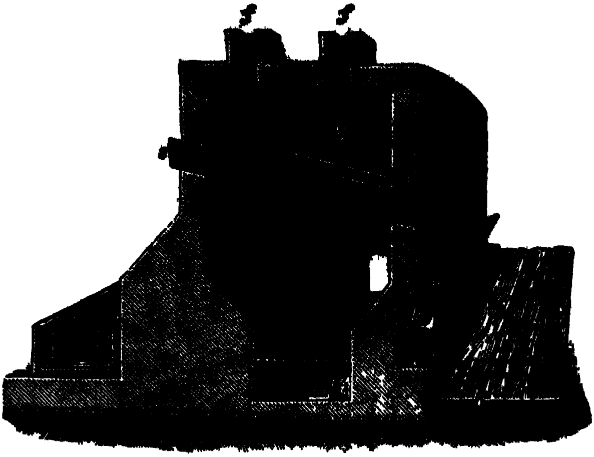

FIG. 273.

re-charged with fresh ore. In a furnace of this kind at Schneeberg, in Saxony,[1] bismuthic cobalt and nickel ores containing up to 12 per cent. of bismuth were liquated. The charge for a tube amounted to 22 to 31 lbs., the liquation of which took from 15 to 20 minutes; the fuel consumption of such a furnace was equal to 590 cubic feet of firewood in 24 hours. The residues still retained one-third of the bismuth present in the ore, and were smelted, forming a bismuthic speiss from which another portion of bismuth was extracted by liquation upon liquation hearths.

The furnace, as modified by Günther, is shown in Fig. 274.[2] The residues can be more easily removed from this furnace than from the Plattner furnace. The tubes are furnished at their lower end with a grating *g*, *g*, made of 7 cast-iron bars, upon which the ore rests. The tubes are charged from their upper end after the cover, *n*, is removed. The heat generated upon the fire-grate *B* melts the bismuth which flows through the spaces between the bars of the grating, *g*, *g*, to the opening *f*, through which it runs out into iron moulds *l*, standing in front of it. The residues are removed from the lower end of the tubes. For this purpose the cover, which is movable about a hinge *q*, is lifted up, and the residues are drawn out over the grating on to an iron plate lying in front of the tube.

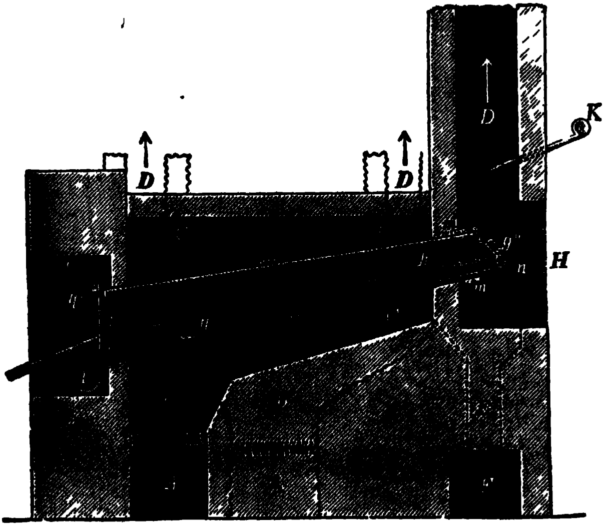

FIG. 274

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[1] Plattner, *Huttenkunde*, p. 23.

[2] Kerl, *Metallhüttenkunde*, p. 530.

The Extraction of Bismuth by Processes of Fusion

For the extraction of bismuth by complete fusion, crucible furnaces are best employed. Shaft furnaces have not given satisfactory results because the bismuth rapidly destroys the walls, penetrates into them in consequence of its fluidity, and is slagged off in considerable quantity. The author does not know whether reverberatory furnaces have ever been used for the extraction of bismuth from ores carrying the native metal. If the native ores contain sulph-arsenides of cobalt and nickel and bismuthic sulphide, the ores are calcined before fusion in order to remove the sulphur and a portion of the arsenic. In order to complete the decomposition of the sulphide of bismuth, iron is added during the process of fusion. Carbon is added for the reduction of the bismuthic oxide, and soda, felspar, lime, quartz or slags may be added to slag off the gangue. At the cobalt works of Oberschlemma, near Schneeberg, ores of bismuth containing cobalt and nickel are first calcined to remove the sulphur and arsenic and then smelted in the smalt furnaces with carbon, iron and slags, producing, together with metallic bismuth, a speiss containing arsenic, iron, nickel and cobalt, and slag. The molten mass is poured into iron pans, in which bismuth separates out at the bottom, over it the speiss and the slag on the top. After the speiss and slag have solidified, the bismuth, which remains fluid in consequence of its low melting point, is tapped off from the solidified substances.

At Joachimstahl, in Bohemia, ores containing lead, nickel, cobalt, uranium, silver, iron, arsenic, sulphur and gangue, with an average of 10 per cent. of bismuth, used to be treated by fusion in Hessian crucibles in charges of 1 cwt., mixed with soda (15 to 50 per cent.), lime (5 per cent.), fluorspar (5 per cent.), and iron turnings (28 per cent.) under a cover of soda equal to 5 per cent. of the weight of the ore. The fusion was effected in an air furnace, charcoal being used as fuel. The slag that formed was removed from time to time, a corresponding quantity of fresh charge being introduced. The products were slag, bismuth and speiss. In 24 hours 2 to 3 cwts. of ore were treated. The crucibles lasted 3 to 4 days. Subsequently the process of fusion was preceded by one of calcination, the ores in quantities of 4 to 10 cwts. being calcined for a period of 4 to 6 hours in reverberatory furnaces fired with lignite. When so much of the slag had been ladled out from the crucible that the entire contents consisted of bismuth and speiss, the latter were poured into conical iron moulds, at the bottom of which the bismuth was deposited. After the mass [illegible] solidified, the bismuth was knocked off from the speiss and freed from any adhering speiss and other difficultly fusible impurities by liquating in iron tubes. The bismuth contained lead, and was freed from this metal by cupellation. The slag contained uranium, and was treated for the production of compounds of this metal. Since the year 1868, the ores from Joachimstahl have been treated at the smelting works in Saxony.

b. The Extraction of Bismuth from Bismuth Glance

Bismuth glance is generally found intermixed with native bismuth. It but rarely occurs in such quantities as to form the material of a separate process for the extraction of bismuth. This is, however, the case with bismuthine occurring in Bolivia. When it occurs intermixed with native bismuth, the ores in question are smelted, either raw or after previous calcination, with a certain quantity of iron, as has been explained under the extraction of bismuth from the ores of Schneeberg and Joachimstahl which contain native bismuth. Ores containing bismuthine alone can either be treated by calcination and fusion with carbon, or in the raw state by fusion with iron. In the one case the chemical processes are the same as in the extraction of lead from galena by the process of calcination and reduction; in the other case the same as in the extraction of lead by the precipitation process. It must be noted that when bismuthic sulphide is calcined, a certain quantity of sulphate is always formed, and this salt is only imperfectly decomposed when the temperature is raised, so that there is always a certain quantity of it present in the charge. It is reduced in the fusion to bismuthic sulphide, which passes into the matte, or into the slag if only very small quantities of matte are produced. When ores contain considerable quantities of gangue, the bismuthine may be separated from it by a simple fusion without the addition of iron. Valenciennes[1] has made experiments upon the extraction of bismuth from bismuthine from Bolivia, which is at present being treated in England. The ores, which occur in Bolivia in considerable quantities, consist of a mixture of sulphides of bismuth, copper, iron, antimony and lead, with small quantities of sulphide of silver. The amount of bismuth in them varies from 15 to 30 per cent. The best process for their treatment has been found to be calcination and reduction. The crushed ores were calcined for 24 hours in a reverberatory furnace with frequent rabbling and intermixture from time to time with crushed coal, and were then smelted in a reverberatory smelting furnace, the calcined ore being mixed with 3 per cent. of coal, lime, soda and fluorspar. In order to assist the reduction, a reducing flame was kept up for the first two hours, the temperature being a red heat, which was subsequently raised to whiteness. The operation was finished as soon as the contents of the furnace were completely fluid. Together with metallic bismuth, a copper matte containing bismuth and slag were obtained. The molten contents were tapped off at the lowest point of the hearth, and run into conical iron moulds placed in front of the furnace, in which they separated according to their specific gravity, the bottommost layer consisting of metallic bismuth, the next of bismuthic copper matte, and the topmost one of slag, consisting chiefly of ferrous silicate. The metallic bismuth still contained lead, antimony and copper, and had to be purified before it could be used for pharmaceutical purposes. The copper matte obtained contained 5 to 8 per cent. of bismuth. It was crushed, calcined, and then smelted in the same way as the calcined ore, the products being metallic bismuth and a copper matte which still retained 2 to 3 per cent. of bismuth. Pure bismuth could not be obtained from the latter in the dry way, an alloy of copper and bismuth being always produced, so that the bismuth had to be extracted from this matte by wet methods. Valenciennes employed precipitation processes in reverberatory furnaces experimentally upon these ores, which he had freed from their gangue by a previous fusion. The ores thus prepared, which consisted only of sulphides of bismuth, iron and copper, were crushed, mixed with 12 per cent. of iron turnings, 30 per cent. of slag, and a certain quantity of soda, and then fused in reverberatory furnaces. After heating for 4 hours up to whiteness, the mass was completely fluid, and was tapped out into conical cast-iron moulds, the products being metallic bismuth, a matte consisting of the sulphides of copper and iron, and slags. The bismuth contained less copper than that obtained by the process of calcination and reduction, but contained antimony. The process worked well, and was much more rapid than the previous one, but had the very great objection that the sulphide of iron rapidly destroyed the hearth of the reverberatory furnace, in consequence of which it was given up.

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[1] Note rélative à la Métallurgie du Bismuth, *Bull. Soc. Chim.*, 1874.

c. The Extraction of Bismuth from Ores which contain it in the Form of Oxide

Oxidised bismuth ores only occur exceptionally in sufficient quantities to be treated by themselves for bismuth. As a rule, they are mixed with native bismuth and are treated together with it. They can be treated by being fused in crucibles or reverberatory furnaces mixed with charcoal. Shaft furnaces cannot be recommended on account of the excessive loss of bismuth, due to slagging and volatilisation. Considerable quantities of hydrated carbonate of bismuth have been found at Meymac, in France. These have, however, been treated by means of the wet method. If the ores containing native bismuth contain at the same time oxides of bismuth, a corresponding quantity of carbonaceous matter is added during the fusion so as to reduce the oxide of bismuth, the carbon dioxide and water being driven off from the above-named compounds by the action of heat.

ii. EXTRACTION OF BISMUTH IN THE DRY WAY FROM METALLURGICAL PRODUCTS

Bismuth is at present generally obtained from metallurgical products by means of the wet methods. We must distinguish in extraction by the dry way:—

(*a*) The extraction from mattes.
(*b*) The extraction from alloys.

a. The Extraction of Bismuth from Mattes

Bismuth is extracted from mattes by methods based on the principle of calcination and reduction. The matte is crushed, calcined in reverberatory furnaces until the bismuthic sulphide is converted into oxide and sulphate, and then smelted with the addition of carbon and suitable fluxes in reverberatory or crucible furnaces. Metallic bismuth is obtained, and, when copper is present in the matte, a copper matte containing bismuth, together with ferriferous slag. As it is not possible to completely decompose the sulphate of bismuth produced during calcination by any increase of temperature, a certain quantity of sulphide is always reproduced during the reduction, which passes into the matte. If only small quantities of matte are formed, this, together with any sulphide of bismuth, passes into the slag. A simple precipitation process is not to be recommended for matte, especially when the latter only contains small quantities of bismuth. The method of treating the matte produced in smelting Bolivian ores has already been explained.

b. The Extraction of Bismuth from Alloys

Alloys from which bismuth can be obtained in the dry way, and from which it used formerly to be so obtained, are its alloys with lead, and with lead and the precious metals. When a lead-bismuth alloy is submitted to an oxidising fusion, the lead is first oxidised, the bismuth only commencing to oxidise when the greater proportion of the lead has been removed. The cupellation of a lead and bismuth alloy can therefore be so conducted that the first product is litharge, the next litharge containing bismuth, and the last, if the oxidation is stopped at the right moment, metallic bismuth. Such a cupellation process was formerly employed at Joachimstahl for the extraction of bismuth. The lead bismuth alloy was cupelled in quantities of 4 to 5 cwts., the first product being litharge free from bismuth, which was sent to the lead works, then a brown litharge containing bismuth, and finally a black oxide of bismuth free from lead, on the appearance of which the metallic bismuth, then free from lead, was tapped into cast-iron pans. The litharge containing bismuth was smelted in crucibles together with the cupel bottoms with a flux consisting of quartz, fluorspar and iron turnings, the product being an alloy of lead and bismuth, which was again submitted to cupellation. The oxide of bismuth free from lead was smelted under a cover of salt with a mixture of quartz, lime and iron turnings. From work-lead containing bismuth, litharge rich in bismuth is obtained in the processes of cupellation in the last stage of litharge production. When this litharge is submitted to a reducing fusion, an alloy of lead and bismuth containing some silver is obtained. By cupelling the latter, litharge still richer in bismuth is obtained, together with litharge free from bismuth, and blicksilver. The former can again be reduced and the alloy of bismuth, silver and lead, thus obtained, can again be cupelled. On reducing this litharge containing bismuth, bismuth containing both lead and silver is obtained. At present, after the argentiferous litharge has been sufficiently enriched in bismuth, it is treated in the wet way.

EXTRACTION OF BISMUTH BY THE WET WAY

Bismuth can be obtained by means of wet methods from ores which contain the metal as carbonate or oxide, and especially from metallurgical products in which the bismuth is in the form of an oxide or an alloy. When bismuth is present as oxide it is generally dissolved by hydrochloric acid, more rarely by nitric acid, which is far dearer; when it is present as metal or alloy, by means of aqua regia or of hot concentrated sulphuric acid.

Bismuth is precipitated from the solutions either directly or as a basic salt. It is generally thrown down as metal by means of iron. As a basic salt it can be thrown down by diluting solutions of its chloride with water, when an oxychloride is precipitated. From the oxychloride bismuth can be reduced either by fusion with lime and charcoal, or by treating the moist salt with iron or zinc. The addition of lime is necessary when the oxychloride is treated in the dry way, in order to combine with the chlorine. The lime may be used either slaked or as caustic lime. Metallic bismuth thrown down in the wet way is melted in graphite or iron crucibles with the addition, in case of need, of alkaline fluxes.

Extraction of Bismuth in the Wet Way from Ores

The wet way has been employed for oxidised bismuth ores at Meymac and for calcined tin ores rich in bismuth at Altenberg in Saxony. The ore treated at Meymac[1] is a hydrated carbonate of bismuth in a quartzose gangue containing small quantities of arsenic, antimony, lead, iron and lime. The crushed ore is treated 3 times over in earthenware vessels with hydrochloric acid at a gentle heat and under constant stirring. The nearly exhausted ore is treated with fresh hydrochloric acid, whilst the almost saturated acid is allowed to act upon fresh ore. saturated solutions being thus obtained, whilst the bulk of the bismuth is removed from the ore. The bismuth is thrown down from the solution in the form of black powder by means of bars of iron. Immediately after its precipitation, it is separated from the solution, washed with water, pressed in canvas bags, and finally melted in graphite crucibles under a layer of charcoal, and cast in iron moulds. At Altenberg, in Saxony, calcined tin ores are treated with hydrochloric acid, which dissolves the oxide of bismuth formed during calcination. From the solution thus obtained, basic chloride of bismuth is thrown down by the addition of water. The precipitate is treated for metallic bismuth. The method of extracting the metal is not indicated in the literature of the subject.

Extraction of Bismuth in the Wet Way from Furnace Products

The chief metallurgical products from which bismuth is extracted in the wet way are impure oxides of bismuth, litharge containing bismuth, and cupellation residues containing bismuth, such as are obtained during the cupellation of alloys of lead, bismuth and silver. Attempts have also been made to treat alloys of lead, bismuth and silver directly in the wet way. When work-lead containing bismuth is cupelled, litharge free from bismuth is first obtained. When the cupellation is continued, the bismuth is also oxidised and passes into the litharge, the last portions of the litharge being richest in bismuth, whilst a small portion of the latter metal remains in the silver. By smelting the last litharge, which contains both bismuth and silver, in shaft furnaces with charcoal, bismuth can be concentrated in the work-lead thus obtained, and by cupelling the latter, litharge still richer in bismuth is produced. The concentration of bismuth in litharge may be brought about simply in cupelling lead which is not too poor in silver, by not continuing the cupellation until the silver brightens but interrupting the process when the silver contents of the work-lead have been enriched to about 80 per cent.[1] In this case the bismuth is concentrated in the alloy produced, and when the latter is finally cupelled upon a smaller hearth, it passes into the litharge and a portion of it into the test. Both litharge and test are so rich in bismuth that they can be treated directly by wet methods. At Freiberg, in Saxony, argentiferous lead containing minute quantities of bismuth is split up by the Pattinson process into lead rich in silver (containing 2 per cent.) and carrying bismuth, and into lead poor in silver (containing 0·1 per cent.) and free from bismuth, the latter of which is then desilverised by means of zinc. The lead containing bismuth is concentrated in German cupellation furnaces until the silver contents reach 80 per cent., and then refined in silver refining furnaces in quantities of 0·9 to 1·2 tons for the production of fine silver, lead and bismuth being thereby oxidised. The oxides are partly absorbed by the hearth, which is made of marl, and partly flow off as litharge containing bismuth. The litharge and the hearth generally contain from 5 to 20 per cent. of bismuth, and are crushed fine and then treated with hydrochloric acid in stoneware pots 30 inches high and 36 inches in diameter, the charge for a pot amounting to 1 cwt. To this are added 140 to 155 lbs. of hydrochloric acid and 22 lbs. of water, the action of the acid being promoted by gently heating and continual stirring. In 6 hours the bismuthic oxide, together with a small portion of lead oxide, has been dissolved, the residues consisting of chloride of lead and metallic silver. Water is added until the liquid becomes turbid owing to the separation of bismuthic oxychloride. The solution is then allowed to stand for 7 hours in order to clear, and is drawn off by means of leaden syphons into wooden vats 6 feet high and 5 feet in diameter, in which it is diluted with a sufficient quantity of water to throw down the bulk of the bismuth as basic oxychloride. As soon as the precipitate has settled, the solution is run off first into settling tanks, and then into a sump in which the copper which it contains is thrown down by means of iron. The precipitate of bismuth oxychloride is then washed with water in a wooden vat provided with a linen filter in order to remove a portion of the chloride of lead. It is then dissolved in hydrochloric acid in order to remove a further portion of chloride of lead. On dilution of the solution with water the bismuth is again thrown down as oxychloride, the latter being again treated with hydrochloric acid in order to remove any portion of chloride of lead that might be left, and from the solution thus obtained the oxychloride of bismuth is again thrown down with water. The salt is then filtered off, washed and dried, and smelted with lime and charcoal or with soda, glass and charcoal in a cast-iron crucible heated in an air furnace, coke being the fuel used. The products are metallic bismuth and slag. The cast-iron crucible is provided with a foot and is 20 inches high in the clear, its greatest diameter being 12 inches. The charge consists of 28 to 44 lbs. of bismuth salt, 16 per cent. of caustic lime, and 6 per cent. of finely ground charcoal. As soon as the contents are in a state of tranquil fusion the slag is ladled off and the bismuth poured into moulds. It is purified by re-melting. It then contains 0·3 to 0·4 per cent. of lead and 0·025 of silver. The residues which remain when the litharge and the various precipitates of bismuthic oxychloride are treated with hydrochloric acid, are washed with water containing hydrochloric acid, dried, and added to charges containing lead and silver, which are being smelted for work-lead.[1] At the St. Andreasberg Works in the Upper Harz, litharge containing bismuth is produced which is sold to Freiberg for treatment in the wet way. At Frankfort-on-the-Maine, in the works of the German Gold and Silver Refinery, bismuth is prepared in the wet way from skimmings containing bismuth, which are obtained in silver refining.

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[1] Carnot, "Découverte d'un Gisement de Bismuth en France," *Bull. Soc. Chim.*, 1874

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[1] Vol. i., p. 579.

Processes for extracting bismuth from alloys in the wet way have been proposed by Mrazek and De Luyne, as to the practical execution of which nothing is known. Mrazek[2] proposed sulphuric acid as the solvent for bismuth contained in argentiferous lead and bismuth alloys. These alloys, which are obtained by repeated reduction and cupellation from litharge containing bismuth, and which contain 50 to 60 per cent. of bismuth, are to be treated in the granulated state with hot concentrated sulphuric acid. Bismuth and silver are thereby dissolved, whilst the lead remains as sulphate in the residues. The silver is to be thrown down from the solution by means of sodic chloride, and the bismuth by means of iron. If alloys of lead and bismuth alone are to be operated on, the bismuth can be thrown down directly by means of iron after the treatment with concentrated sulphuric acid. The spongy bismuth obtained by this means is to be pressed, dried, and then melted. The proposed process of De Luyne[1] refers to the extraction of bismuth from alloys containing tin, lead and bismuth. These are first to be treated with cold hydrochloric acid, so as to remove the greater portion of the tin. The bismuth is then to be brought into solution by treating the residues with aqua regia, and from this solution the bismuth is to be thrown down as oxychloride by dilution with water. This salt is either to be smelted in crucibles for metallic bismuth, in admixture with chalk and charcoal, or it is to be dissolved in hydrochloric acid and the metal thrown down by treating the solution with zinc and the precipitate pressed, dried and melted. Another proposed process of De Luyne suggests the employment of nitric acid as a solvent, which dissolves bismuth and lead, whilst the tin is converted into an insoluble oxide; from this solution the bismuth is first to be thrown down as metal by means of lead, and then the lead precipitated as carbonate by means of sodic carbonate.

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[1] *Preuss. Zeitschr.*, vol. xviii., p. 193; *Berg. und Hütt. Ztg.*, 1876, p. 79.

[2] *Oesterr. Zeitschr.*, 1874, Nos. 34 and 35.

EXTRACTION OF BISMUTH FROM LEAD-BISMUTH ALLOYS BY THE ELECTROLYTIC METHOD

Borchers has proposed the extraction of bismuth from lead containing it, by means of the electric current, and has devised apparatus for this process. He fuses alloys containing lead and bismuth, or lead, bismuth and silver, under molten alkaline chlorides, through which he passes an electric current. The lead is dissolved as chloride and is deposited as metal at the cathode or at the bottom of the cathode compartment, whilst with a suitable current density, bismuth and silver remain undissolved and collect at the bottom of the anode compartment. Although the process has not come into use, an explanation of the process and mode of working as communicated by

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[1] *Dingler*, vol. 167, p. 289.

Borchers may be of interest.[1] The construction of the apparatus is shown in Figs. 275 to 277, the first showing the plant and the empty apparatus with the cover removed, Fig. 276 being a vertical cross section, whilst Fig. 277 shows the left hand half in vertical longitudinal section, and the right hand half of the apparatus in elevation. *The fusion is performed in a vessel of cast iron, which consists of two* horizontal semi-cylinders *a* and *k*, and a hollow iron frame *v* in the shape of a semicircle. The semi-cylinder *a forms the anode compartment*; its left-hand end is steeply inclined. The sides of the anode compartment are provided with a series of step-like projections. The semi-*cylinder k forms the cathode compartment*, the right-hand side of which is also inclined. The hollow iron frame or iron ring *v* separates the anode from the cathode departments Water circulates in it during the electrolysis and cools its walls to such an extent that they are coated externally with a layer of solidified alkaline chlorides, which serves to insulate it. The anode and cathode compartments are thus insulated from each other by means of this ring. The water enters the ring through the tube *e* and escapes at *x*. Should anything happen to prevent the circulation, an overflow is provided at *s* until it can be put right. The outer circumference of this iron ring is provided with hollow projections which give it the form of an inverted *T* in cross section. The hollow space between these two semi-circular projections is filled with an insulating material consisting of clay free from carbonaceous matter, sand and marl. These projections also serve to carry the flanges *f*,*f* of the two semi-cylinders and thus to unite the various portions of the apparatus. The tubes *p* and *r* serve to regulate the level of the molten mass and to remove the metals after their separation from each other. By means of the pipe *r*, which opens into the bottom portion of the anode department, the bismuth is to be removed, whilst the lead is to flow off through

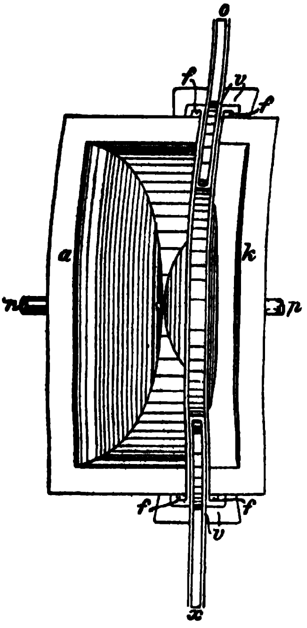

Fig 275.

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[1] *Jahrb. der Electrochem.*, 1895, p. 168.

the tube *p*, which [illegible] compartment. The flame, [illegible] the flues *h* which surround this vessel and then [illegible].

The process is as follows:—As soon as the water is flowing through the cooling ring *v*, firing is commenced, and sufficient lead is poured in

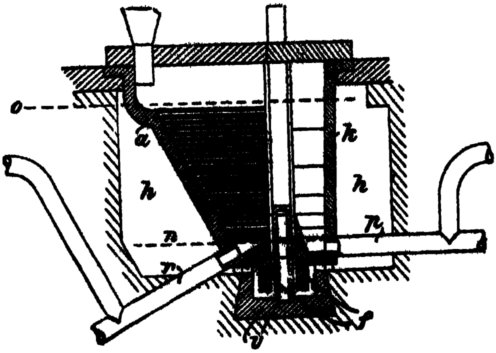

FIG 276.

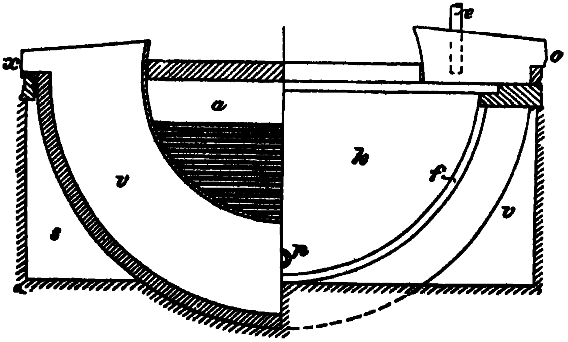

FIG 277.

through the pipes *p* and *r* to partly fill the anode and cathode departments. A mixture of alkaline chlorides in the ratio of their molecular weights KCl + NaCl is then charged. As this mixture melts but slowly it must only be introduced in small quantities at a time. It is better, however, to fuse the mixture in a separate pot and to allow the molten mass to run all at once into the decomposing pot. In order to prevent the iron of this vessel, especially at the anodes, from being attacked by the fused mass, it is necessary to make it basic by dissolving in it litharge, or better still lead oxychloride. These lead compounds must, however, only be added after the pot has been filled with the fused mass, because, otherwise, lead would be deposited upon the metallic portion of the pan, penetrate through the insulation, and thus cause short circuiting. After the pot has been filled with the molten mass, and the external portions of the cooling ring and the iron in its immediate neighbourhood have become covered with a crust of non-conducting and irreducible salts, then the lead compounds have a most beneficial effect upon the electrolysis, and it is preferable to replace the potassium chloride that is volatilised by lead oxychloride. As soon as the first charge of lead compounds has been added, the alloy of lead and bismuth is introduced into the anode department by means of a funnel and a current passed through the molten mass. The molten alloy runs down over the step-like projections of the side of the anode department, and the lead in it is dissolved and re-deposited in the cathode department, on the bottom of which it collects. On the other hand, bismuth and silver remain undissolved as long as the current tension does not exceed 100 ampères per square foot, and collect at the bottom of the anode compartment. The lead thus obtained is very pure and is tapped off from time to time through the pipe *p*. The crude bismuth contains 90 to 95 per cent. of bismuth and is tapped off from the pipe *r*. The upper apertures of the pipes *p* and *r* must be so arranged that the molten salts reach up to the line *o*, the molten lead up to the line *n*. The bismuth produced contains lead, which can however be readily removed by means of an oxidising fusion. In order to obtain a good separation, it is necessary that the molten alloy should continually present fresh surfaces, so that it is necessary for it to traverse the anode compartment pretty quickly. Complete decomposition is therefore only effected after it has passed through the apparatus several times. Several of these apparatus must therefore be employed placed stepwise, one below the other, or else the alloy must be caused to pass several times through the same apparatus. With a current density of 100 ampères per square foot the tension required is said to amount to 0·5 volt. Accordingly about 10 lbs. of lead can be separated from the alloy per horse power per hour. As already stated, this process, which is said to work without any loss of metal, has not yet come into use.

REFINING OF BISMUTH

Bismuth produced in the dry way contains arsenic, sulphur, iron, nickel, cobalt, antimony, and also silver and gold. The following are analyses of two samples of crude bismuth :—[1]

	Peru.	Australia.
Bismuth	93·372	94·103
Antimony	4·570	2·621
Arsenic	—	0·290
Copper	2·058	1·944
Sulphur	—	0·430

The amount of gold and silver contained in various qualities of bismuth has been determined by Smith.[2] He found 0·011 per cent. of gold and 0·3319 per cent. of silver in a sample of Australian bismuth; 0·0003 per cent. of gold and 0·0729 per cent. of silver in a sample of German bismuth; and 0·0005 per cent. of gold and 0·075 per cent. of silver in a sample of American bismuth. Impure bismuth is not suitable for many purposes for which the metal is employed, and must therefore be purified before use. When it is to be used for pharmaceutical purposes it must be especially pure and, above all things, free from arsenic and tellurium. The purification of bismuth can be performed either in the dry or in the wet way. The dry method produces a metal less pure than the wet way, and in the case of bismuth which contains a number of foreign bodies is a very lengthy process, as these cannot be removed by one single operation, but require a whole series. It has the advantage that it is far cheaper than the wet method, which is also a very roundabout one and only used in special cases.

Purification of Bismuth in the Dry Way

This may consist either in a liquation process or in re-melting bismuth with fluxes of various kinds. Liquation of bismuth is employed in Saxony. It is performed upon a liquation hearth consisting of cast-iron segments forming a groove inclined outwards; the liquated bismuth is cast, just before setting, into iron moulds. Any sulphide of bismuth that may be present then separates out upon the surface of the blocks. The residues that are left upon the liquating hearth, known as *Krätzen*, contain the greater portion of the impurities of the bismuth, and are treated for the extraction of the metals contained in them. If the bismuth is required for pharmaceutical purposes liquation is not always sufficient, and the metal may require further purification by melting or by the wet method.

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[1] *The Mineral Industry*, 1893, p. 72.

[2] *Journ. Soc. Chem. Ind.*, April 29, 1893, p. 318.

The purification of bismuth by remelting in crucibles with various additions is much more perfect than the purification by liquation, but even this is not sufficient in all cases. It must then be repeated until the bismuth is pure. The fluxes that are added depend upon the impurities that have to be removed. According to Quesneville arsenic can be removed by melting bismuth with nitre and common salt. This process, the object of which is to form alkaline arsenites, also removes iron and lead. According to Werther, arsenic may be removed by fusing bismuth with one-eighth of its weight of soda and one-sixty-fourth of sulphur. In both methods a considerable loss of bismuth is incurred by the formation of bismuthic oxide. According to Thürach arsenic, and more particularly the whole of the iron, may be removed by fusing bismuth with chlorate of potash to which from 2 to 5 per cent. of soda has been added. According to Méhu, arsenic may be removed from bismuth by heating the latter considerably above its melting point with excess of air in a vessel presenting a large surface. The greatest part of the arsenic is thus removed as arsenic acid, and any sulphur that may be present is converted into sulphur dioxide. The residue has to be remelted with soda, charcoal and tartar or soap, producing an alkaline mass which, when further heated in the air, is freed from the last portions of arsenic and sulphur, which combine with the alkali. In this process any copper and lead will remain in the bismuth. Johnson, Matthey and Co. heat bismuth[1] containing arsenic in quantities of 10 to 12 tons to a temperature of 395° C. for a considerable time in the air, whereby the whole of the arsenic is volatilised without loss of bismuth. Tamm removes arsenic by dipping thin strips of iron into the bismuth fused beneath a layer of borax at a bright red heat. The arsenic is said then to combine with the iron, and to be completely removed from the bismuth as arsenide of iron. A small portion of iron is, however, retained in the bismuth. Johnson, Matthey and Co.[1] remove antimony by poling the bismuth, which is heated up to the oxidation point of antimony, by means of a piece of wood, the scum produced being removed as long as any forms upon the surface of the bath of metal. For example, 7 cwts. of the molten metal which contained 96·2 per cent. of bismuth, 0·8 per cent. of antimony, 0·4 per cent. of iron, 2·1 per cent. of lead,

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[1] Matthey, *Chemical News*, 1893, pp. 63–67.

0·5 per cent. of copper, and a trace of arsenic, were heated for 4 hours in the above manner to a temperature of 455° C., at the end of which time the bismuth was free from antimony. The scum contained 30 per cent. of antimony as oxide, and about 10 per cent. of bismuth. Antimony may, moreover, be completely removed by melting bismuth with bismuthic oxide in clay crucibles. The quantity of oxide should be from 2½ to 3 times that of the antimony to be removed. The bismuthic oxide oxidises the antimony to oxide, being itself reduced to metal. The oxide of antimony mixed with a small portion of oxide of bismuth rises to the surface of the bath of metal and is skimmed off it. Borchers[1] removes arsenic (after lead has been removed by melting with caustic soda, sodic and potassic chlorides, and bismuth oxy-chloride) by melting the metal with caustic soda and nitre, care being taken to avoid overheating; he only melts with soda and sulphur when a considerable proportion of antimony is present. According to Tamm, copper can be removed by melting bismuth with potassic sulpho-cyanate. For this purpose 8 parts of potassic cyanide are mixed with 3 parts of flowers of sulphur and the mixture is thrown on to the molten metal. Potassic sulpho-cyanate is formed with an evolution of heat, so that the compound burns in part, throwing out sparks, the copper separating out in the form of sulphide: any bismuthic sulphide that may be formed is reduced to metal. As soon as the re-action is over and the mass is in a state of tranquil fusion, the slag is allowed to solidify and the still fluid bismuth is poured off. Together with the copper a portion of the lead, antimony and arsenic are removed. Copper is also said to be removed by melting the bismuth with bismuthic sulphide, the latter being reduced to metal.[2]

The best method of removing the copper is said to be by stirring sodic sulphide into the molten bismuth, whereby the copper is also separated in the form of sulphide.[3] According to Borchers[4] lead can be removed as soon as the quantity exceeds the fraction of a per cent. by heating the metal with bismuthic oxychloride in quantity corresponding to that of the lead present, in cast-iron kettles under a molten layer of the chlorides of sodium and potassium for a period of 3 hours. As soon as a sample of the metal sets showing coarse foliation, the refining is finished. After the solidification of the metal the slag is removed by dissolving in water. Borchers considers the removal of lead by melting the metal with caustic soda and nitre, as has often been recommended, to be defective, because plumbates are formed, which being good oxygen carriers, give rise to losses of bismuth. If, on the other hand, the bismuth is free from lead, but still retains arsenic and antimony, these bodies are to be removed by melting the metal with caustic soda and nitre. According to Phillips[1] the Pattinson process is said to separate lead from bismuth with a considerable degree of perfection, the lead passing into the crystals. According to Méhu sulphur can be removed in great part by heating the bismuth above its melting point with excess of air, whereby the former is oxidised to sulphur dioxide. The remainder of the sulphur may be removed by melting the metal containing oxide of bismuth with soda, charcoal and tartar or soap. According to Tamm it may also be removed by melting bismuth with wrought iron. Gold may be extracted from molten bismuth by the aid of zinc. Silver can be removed in the same way. The bismuth may be freed from zinc, according to Mrazek, by the aid of air. If copper, arsenic, antimony and sulphur are all present in the bismuth, Tamm recommends to remove first the copper, then the antimony, and finally arsenic and sulphur.

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[1] *Electro-metallurgie*, 1895, p. 328.

[2] *Proc. Royal Soc.*, vol. xlii., p. 89.

[3] *Tech. Chem. Jahrb.*, 1890–91.

[4] *Op. cit.*, p. 328.

Purification of Bismuth in the Wet Way

This method is dearer than the dry way, but yields on the other hand a purer product. It is only employed when a basic bismuth nitrate is required for medicinal purposes, or when the metal is to be prepared for use in the laboratory. Herapath's process has for its object the preparation of basic bismuthic nitrate free from arsenic. He dissolves bismuth in nitric acid, precipitates the basic nitrate by diluting the solution with water, boils the residue with caustic potash or soda to remove arsenic or lead, washes the oxide thus obtained, redissolves in nitric acid, and again precipitates the basic nitrate from the solution by means of water. Deschamps produces pure bismuthic nitrate by dissolving the bismuth in nitric acid, any tin or tin oxide thus remaining in the residue, treating the solution with ammonia, which throws down bismuth whilst copper and silver remain in solution, boiling the precipitate with a solution of caustic potash, whereby lead and arsenic are dissolved, and dissolving the precipitate in nitric acid, and precipitating the basic nitrate by means of water. Schneider dissolves bismuth in nitric acid heated to between 75° and 90° C., whereby the whole of the arsenic present separates out in the form of arseniate of bismuth with some basic bismuthic nitrate. (When cold nitric acid is employed, arsenite of bismuth is formed, which is difficultly soluble in nitric acid, and quite insoluble in bismuthic nitrate.) The solution thus obtained is separated from the residues by filtration through an asbestos filter. The clear solution is evaporated, when crystals of nitrate of bismuth perfectly free from arsenic separate out. Hampe has proposed a process for the preparation of pure bismuth for chemical purposes. He melts bismuth with a mixture of sodic carbonate and sulphur, producing bismuthic sulphide, which is dissolved in nitric acid after thorough washing; he precipitates the basic nitrate by the addition of water, dissolves it again in nitric acid, and treats the solution with excess of ammonia for the precipitation of bismuthic oxide. The precipitated bismuthic oxide is dried and reduced by hydrogen. The composition of purified commercial bismuth is shown in the following analyses of Schneider:—[1]

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[1] *Elements of Metallurgy*, London, 1891, p. 614.

	Bolivia.		Saxony	
	I	II	III	IV
Bi	99·053	99·069	99·390	99·830
Ag	0·083	0·621	0·188	0·075
Pb	-		-	trace
Cu	0·258	0·156	0·090	0·040
Fe	—	—	—	0·026
Sb	0·559	—	—	—
As	—	—	0·255	—
Au . . .	—	trace	—	—
Tl	—	0·140	—	—

BISMUTH PRODUCED IN 1890 IN THE SMALT WORKS OF SAXONY.

	I	II
Bi	99·791	99·745
Ag	0·070	0·066
Pb	0·084	0·108
Cu	0·027	0·019
Fe	0·017	trace
As	—	0·011
S	trace	0·042

SO CALLED COMMERCIAL "BISMUTH PURISSIMUM."

	I	II	III
Bi	99·922	99·849.	99·982
Ag	—	0·047	—
Pb	—	0·049	0·065
Cu	0·016	0·019	0·032
Fe	trace	trace	trace
As	0·025	0·024	trace

Journ. f. Pract. Chem., vol. xxiii., p. 75. *Ibid.*, N.F. xliv. 23-48.

TIN

PHYSICAL PROPERTIES

TIN has an almost silvery whiteness with a slight bluish tinge and a brilliant lustre. The latter depends to a large extent on the temperature at which it is poured; if the temperature were too high, the surface would show iridescent colours, while if poured at too low a temperature the surface would be dull. The admixture of small quantities of foreign metals (lead, arsenic, antimony, iron, bismuth) also diminishes the lustre of tin.

Tin is dimorphous. It crystallises in the forms of the tetragonal and rhombic systems.[1] The tetragonal form is obtained by reduction from a solution of stannous chloride, or by cooling molten tin at the usual temperature of the air. Rhombic tin is produced by a very gradual cooling of molten tin at a temperature slightly lower than its melting point. The structure of tin is distinctly crystalline; if the surface of tinned plate or tinfoil be etched with hydrochloric acid which contains free chlorine, or with stannic chloride, it becomes covered with a pattern resembling frost pictures on windows (*moiré metallique*). A bar of tin emits, when bent, a characteristic creaking noise, the so-called "cry" of tin. This is due to its crystalline structure, the individual crystals grinding against one another on bending.

Some kinds of tin when exposed to severe cold (– 20° C.) acquire a rod-like or columnar structure. At lower temperatures still (– 40° C.), the rods or columns break up into grey friable grains. These small grains from their characteristic colour are known as the *grey modification* of tin. The exact cause of this molecular change is not known; under these conditions (and presumably as the result of them) certain kinds of tin break up, while others are not affected. If a small quantity of the grey modification be hammered into some ordinary tin, the latter in a short time changes into the grey modification.[1] The specific gravity of cast tin is 7·291, of rolled tin 7·299, of electrically deposited tin from 7·143 to 7·178. That of the grey modification varies about a mean of 7·195 (Rammelsberg), while this variety after remelting has a specific gravity of 7·310.

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[1] V. Foullon, *Jahrb. der K. K. Geolog. Reichsanstalt*, 1884, p. 367.

Tin is harder than lead but softer than gold. It is so extensible at ordinary temperatures that it can be beaten and rolled to thin leaf (sheet tin and tinfoil). At higher temperatures its extensibility diminishes, until at 200° C. it is so brittle that it breaks to pieces when hammered, and can be powdered. If the temperature at which tin is cast be either too high or too low, it will be "short," *i.e.* brittle. The addition of 1 per cent. to 2 per cent. of copper or lead increases the hardness and tenacity of tin.

Tin is ductile but possesses little tenacity; it is most ductile at about the temperature of 100° C.; a wire 0·08 inch in diameter breaks under a load of 54 lbs.

The melting point of tin is given differently by different observers:—Creighton, 228°, Rudberg, 228·5°, Kupffer, 232°, Person, 232·7°. It boils at a white heat (between 1600° and 1800°), and burns with a white flame in the air at this temperature, forming stannic oxide. Its linear expansion by heat, according to Calvert and Johnson, between 0° and 100° C., is 0·002717; its specific heat between 0° and 100° C., according to Regnault, is 0·0562; its conducting power for heat is 145 to 152, when silver is taken as 1000 (Wiedemann and Franz); its conducting power for electricity at 21° C. is 11·45 (Mathiessen) or 14·01 (Becquerel), silver being taken as 100.

Tin is usually contaminated by iron, arsenic, antimony, lead, copper, bismuth, tungsten, molybdenum and stannous oxide. The effects of these impurities are:—Iron, if present in considerable quantities makes the tin hard and brittle; arsenic, antimony and bismuth, if present to the extent of 0·5 per cent. reduce its tenacity; copper and lead (1 per cent. to 2 per cent.) make it harder and increase its strength, but make it less malleable; tungsten and molybdenum render it less easily fusible; stannous oxide reduces its tenacity; sulphur is said to render it "short."

THE CHEMICAL PROPERTIES OF TIN AND ITS COMPOUNDS, WHICH ARE OF IMPORTANCE IN ITS EXTRACTION

Tin at ordinary temperatures is not acted on by either air or water. In air, at temperatures above its melting point, it becomes covered with a greyish white film, a mixture of stannous oxide and tin, which by continued heating is changed into a whitish-grey powder of stannic oxide, the so-called "putty-powder" of commerce. The complete conversion into stannic oxide is accelerated by raising the tin to a red heat, and also by the presence of lead.

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[1] *Chem. Zeitung*, 1892, pp. 16, 1197; 1893, pp. 17, 1386.

Tin decomposes steam at a red-heat, being oxidized to stannic oxide.

Tin dissolves in hydrochloric acid with liberation of hydrogen and formation of a solution of stannous chloride; the concentrated hot acid dissolves it briskly; cold, dilute acid, on the other hand, acts very slowly.

Cold dilute sulphuric acid has very little action on tin; the hot concentrated acid however, forms with it a solution of stannous sulphate with evolution of sulphur dioxide.[1]

Ordinary nitric acid, of specific gravity 1.3, oxidizes tin to white hydrated metastannic acid, insoluble in excess of nitric acid; highly diluted nitric acid is reduced by tin with the formation of stannous nitrate and an ammonium salt. The most concentrated nitric acid has no action on tin.

Aqua regia dissolves tin forming stannic chloride; if there be excess of nitric acid present metastannic hydrate is produced.

Warm concentrated solutions of either caustic potash or soda dissolve tin with liberation of hydrogen, forming stannate of potash or soda.

OXYGEN COMPOUNDS OF TIN

We know two compounds of tin with oxygen, stannous oxide, SnO, and stannic oxide or stannic acid, SnO_2. Stannous oxide acts as a base, while stannic oxide acts both as a base and as an acid.

Stannous Oxide, SnO,

is obtained by treating stannous chloride with alkaline carbonates and boiling the resulting white hydrated stannous oxide with water containing a very small quantity of potash, insufficient to dissolve the hydrated oxide. This oxide takes the form of small glistening black crystals, which are not altered by exposure to air at ordinary temperatures, though when heated in the air they take fire and burn, forming stannic oxide.

The hydrated oxide passes gradually in the presence of water into hydrated stannic oxide.

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[1] Recent researches show that stannic, and not stannous, sulphate is formed. See *Journ. Chem. Ind.* 1898, p. 214.

Stannic Anhydride, SnO_2,

is found in nature as *tin stone* or *cassiterite*. It can be produced by heating tin to a high temperature in the air, or by igniting stannous hydrate, or by igniting stannous oxalate.

Stannic anhydride in the pure state possesses a white or straw-yellow colour which on heating changes to a transient brown. This oxide is reduced to the metal by heating it with carbon. It is insoluble in all acids, but dissolves in aqueous solutions of the alkalis.

Stannic Acid, H_2SnO_3,

is prepared as a bulky white precipitate by treating stannic chloride solution with ammonia It is soluble in sulphuric and nitric acids with formation of oxysalts of tin, and in aqueous solutions of the alkalis with formation of salts of stannic acid (stannates).

A modification of stannic acid, the so-called *metastannic acid*, $H_{10}Sn_5O_{15}$, is distinguished by its insolubility in acids. It can be obtained as a white powder by treating tin with nitric acid Ordinary stannic acid is converted by long contact with water into this modification.

CHLORIDES OF TIN

Tin forms two compounds with chlorine: stannous and stannic chlorides.

Stannous Chloride, $SnCl_2$,

is obtained by acting on tin with hot concentrated hydrochloric acid.

Stannic Chloride, $SnCl_4$,

is prepared by dissolving tin in aqua regia, or by passing chlorine through a solution of stannous chloride, or by burning tin in dry chlorine gas.

OXY-SALTS OF TIN

Among these must be mentioned the *sulphate* and the *nitrate* of tin. The former is prepared by dissolving tin in boiling concentrated sulphuric acid. The nitrate is obtained when tin is treated with dilute nitric acid.

SULPHIDES OF TIN

Tin forms two compounds with sulphur, stannous sulphide, SnS, and stannic sulphide, SnS_2.

The *stannous sulphide* is obtained by melting together tin and *sulphur, or by the action of sulphur vapour on finely divided tin. It is a leaden-grey foliated mass with a metallic lustre. It can be obtained as a brown precipitate of hydrosulphide by passing sulphuretted hydrogen through a solution of a stannous oxy-salt or* stannous chloride.

Stannic sulphide can be prepared in the form of golden yellow, glistening scales by heating together tin filings, sulphur and salammoniac; it is known under the name "mosaic gold." The hydrosulphide can be prepared as a yellow precipitate by passing sulphuretted hydrogen through a solution of a stannic oxy-salt or stannic chloride.

Phosphorus and *arsenic* combine with tin directly as well as indirectly, forming silver-white brittle substances.

ALLOYS OF TIN

Tin alloys with most metals in almost any proportion; of these alloys many, on account of their special properties, are applied in the arts. Among them must be mentioned the tin-copper alloys, *e.g.*, bronze, gun-metal, bell-metal; the tin-lead alloys, *e.g.*, pewter, tin-foil, soft solder; the tin-antimony alloys (sometimes with the addition of lead and copper), *e.g.*, bearing-metal, britannia-metal; the tin-bismuth-lead alloys used for type, calico-printing-blocks, and castings; the tin-zinc alloys used for imitation silver leaf; and tin amalgam used for silvering mirrors.

TIN ORES

The only ore of tin which is used for the extraction of the metal is *tin stone* or *cassiterite*, SnO_2, containing 78·6 per cent. of metal. It is found in lodes, stockworks and beds, and also in secondary deposits of water-worn particles, the so-called alluvial deposits. The ores obtained from the former deposits are called *lode-ores*, those from the alluvial deposits, *stream tin*, *washed tin*, *tin-sand*, *black tin*, *barilla.*

The lodes are found in the older rocks, in granite, gneiss, mica-schist, greisen and clayslate, the *cassiterite* being usually accompanied by quartz, mica, fluorspar, apatite, felspar, soapstone, tourmaline, chlorite, topaz, axinite, sulphides of various metals, mispickel, specular iron ore, magnetic iron ore, native bismuth, wolfram and molybdenite.

The alluvial deposits are formed by the weathering of the lodes and surrounding rocks. They are therefore usually found occupying old river beds, and mostly in the neighbourhood of the original lode.

The ores from them are invariably purer, because by the action of the atmosphere and running water, a portion of the injurious impurities, *e.g.*, arsenides and sulphides, have been decomposed and carried away.

Tin ore is found in England, Sweden, Russia (Pitkaranta in Finland and Transbaikalia in Siberia), Saxony, Bohemia, Spain (in the province of Galicia), Portugal (Zamora), France (Morbihan, Vaulois, Cieux, Montebras), in the United States (California, Dakota, North Carolina, Virginia, Alabama), Mexico, Brazil, Peru, Bolivia, Chili, China, the Malay Peninsula, Sumatra, Banca, Billiton, Carimon, Burmah, Siam, Anam, New South Wales, Queensland, Western Australia and Tasmania.

The most important localities which at present furnish a supply of tin ore are, in England, Cornwall and Devon, where the deposits have been worked since the time of the Phœnicians. The alluvial deposits are exhausted and at the present time the ore is obtained from lodes and branches from them into the enclosing rock. Altenberg, Geyer and Zinnwald in Saxony, must be mentioned; in these localities the ore is found in stockworks; also Graupen and Schlaggenwald in Bohemia, where it occurs in similar deposits. The quantity of ore produced in Saxony and Bohemia is small in comparison with that obtained from England, Australia and the East Indies. In France, tin stone is found in Brittany (at Villeder and Piriac) and in Creuse (at Montebras), but only in small quantities; also in small quantities in Spain (in Galicia).

Beyond the continent of Europe the most important localities where tin has been discovered are:—in the East Indies (alluvial deposits), Banca, Billiton, Sumatra, the Carimon Islands, the Malay Peninsula; in Australia, both alluvial deposits and lodes are found in New South Wales and Queensland. The most important Australasian locality is Mount Bischoff in Tasmania, where the ore is found in alluvial beds, in lodes, and in stockworks or pockets. A dyke of eurite and porphyry having broken through the Silurian shales and sandstones, these latter are, at their contact with the dyke, all cracked and fissured, and the fissures are filled with tin ore, and arsenical and copper pyrites. These sulphides increase in quantity with depth.

Tin is also found widely disseminated in Bolivia at Chorolque, Oruro, Potosi and Porco.

The greatest amount of stream tin is produced in the abovementioned localities in the East Indies.

Tin stone possessing a fibrous structure is known as *wood tin.*

The mineral *tin pyrites* or *bell-metal ore* may also be referred to here, as it contains tin to the extent of 25 to 28 per cent. It consists of an isomorphous mixture of the sulphides of tin, zinc, iron and copper; the only place where crystals of it have been found is Huel Rock, St. Agnes', Cornwall. On account of its rarity it is not used as a source of tin.

THE EXTRACTION OF TIN FROM THE ORE

The dry method is principally used for the extraction of tin, but wet methods are used in some cases to assist in the separation of certain injurious impurities. Different proposals for the treatment of tinstone by electro-metallurgical methods have been made, but they appear to have no prospect of success. Proposals have also been made for the treatment of tin slags in this way, but it does not appear that there has been any practical application of them so far.

Wet methods as well as electrical methods have been applied to the recovery of tin from refuse, especially from tinned plate cuttings.

The metal obtained from tinstone is nearly always contaminated by foreign elements and therefore needs to be purified from them. This purification, the refining of tin, is done in the dry way; it can, however, be done with the assistance of wet methods.

We have therefore to distinguish:—

I. The extraction of tin in the dry way, subdivided into:—
   A. The extraction of tin from tinstone and from the intermediate products and dross obtained during the process.
   B. The refining of tin and working up of refinery dross.
   C. The extraction of tin from skimmings and other forms of dross.

II. The extraction of tin in the wet way.

III. The extraction of tin by electro-metallurgical methods.

I. THE EXTRACTION OF TIN IN THE DRY WAY

A. THE EXTRACTION FROM TINSTONE

The extraction of tin from tinstone depends upon the reducibility of tin oxide by carbon and carbonic oxide at a high temperature. The reduction only commences at a white heat. If the tin ore be accompanied by oxides of other heavy metals, especially ferric oxide, as is usually the case with lode ores, these are reduced at the same time, part of the reduced metal going to contaminate the tin and part forming furnace *sows* and *bears*. Further, the reduced iron separates the metals from any sulphides present, and these alloy with the tin. Stannic oxide acts as a base to silicic acid, and, therefore, if the latter be present, the tin ore will form with it a very infusible slag. The difficultly reducible monoxide bases (the alkalis and the alkaline earths), towards which stannic oxide acts as an acid, will, if present, likewise form slag. In consequence of the contamination of tin by the heavy metals and the formation of *sows* and *bears*, on the one hand, and the slagging of the tin oxide by silica and alkalis on the other, it is absolutely essential that the tin ore be freed as far as possible from impurities before reduction, whether the latter is to be performed in reverberatory or in shaft furnaces. This is done partly by mechanical dressing of the ores, and partly by the use of chemical means, such as roasting or treatment with acids. The preliminary cleaning of tin ores therefore is an important part of the extraction of tin. It is not practicable, however, to free tin ore completely from its impurities, and it is, accordingly, necessary that the impurities remaining in the ore after the preliminary treatment should be carried away in a suitable slag. Further, it is necessary that even with a pure ore a suitable slag should be produced, in order that the reduced tin, which oxidises very readily on exposure, may be protected. The production of an easily fusible slag (from ferrous oxide and lime) would, for the reasons given above, give rise to the reduction of iron and the slagging of tin oxide by the lime; it is preferable therefore to produce only a porportionally small quantity of a difficultly fusible slag, in doing which it will be impossible to prevent an important quantity of tin being mechanically enclosed. This slag must be freed from its contained tin by resmelting; this prolongs the process and tends to a correspondingly increased expenditure in fuel.

We have therefore under the extraction of tin from tinstone, to consider:—

1. The purification of tinstone from injurious impurities.
2. The reduction of tin ore.

1. THE PURIFICATION OF TINSTONE FROM INJURIOUS IMPURITIES

The purification of tinstone from the greater part of its impurities is readily done by taking advantage of its high specific gravity, its stability at a red heat and its insolubility in acids.

In consequence of the high specific gravity of tin ore, it is possible to remove earths, quartz, silicates, as well as most of the metallic oxides, by mechanical treatment. The stability of tinstone at a red heat allows the hard siliceous pieces of ore stuff to be calcined previous to dressing until they are brittle, and by the oxidation which takes place during the roasting, sulphur, antimony and arsenic are driven off from their compounds in the ore. The insolubility of tin ore in acids permits the removal of bismuth and copper from the roasted ore by means of acids. In many cases the tin ore contains tungsten compounds, such as wolfram $(FeMn)WO_4$, scheelite $CaWO_4$, or tungstite WO_3. When such ore is fused with alkaline fluxes, *e.g.* soda or sodic sulphate, at first tungstate, and afterwards stannate of the alkali are formed. By employing a suitable quantity of fluxes the tungsten can be removed while only a trace of tin is lost as stannate. This method for the removal of tungsten from tin ores was tried, but has been abandoned. The causes of its abandonment are said to be the high cost of the process itself, the restricted market for alkaline tungstates, and the loss of tin by the formation of sodium stannate, and also the disappearance of tungsten from the ore in Cornwall. As tungsten compounds, on account of their high specific gravity, cannot be separated from tin ore by dressing, the separation is effected in many places by hand picking and careful sorting.

With stream tin a mechanical dressing suffices in most cases to produce a pure tin ore; with lode ores, however, roasting, and in many cases solution processes, must be used to assist the mechanical cleaning. If the lode ore contains much quartz or gangue, calcining to render it brittle, and therefore better fitted for crushing, is found useful before the dressing (*Altenberg tin zwitter*).

By the mechanical dressing to which the ore is subjected, either with or without previous calcination, the gangue, earths, quartz and oxides of the heavy metals are for the most part removed, while the sulphides, arsenides and tungsten compounds nearly all remain with the ore.

In order to remove sulphur and arsenic, and also to convert the metals, with which they are combined, into oxides, the ore is subjected to an oxidising roasting, which is followed by a washing to remove the metallic oxides formed during the roasting. If the ore contains a great proportion of arsenic, as is the case in Cornwall, it is subjected to a second roasting followed by another washing, in order to remove the last portions of that impurity. When copper and bismuth are present, the oxides of these metals, which are formed during the roasting process, are extracted by acids before further washing; dilute sulphuric or hydrochloric acid is used for the purpose.

Tungsten used formerly to be removed after the washing by fusion of the ore with soda or glauber salt. By a judicious combination of these processes—dressing, roasting, and lixiviation—the tin contents of the ore can be raised from between 1 per cent. and 2 per cent. to between 50 per cent. and 70 per cent.

The Roasting of Tin Ore

The dressed ore, which still contains sulphides and arsenic compounds, principally iron and copper pyrites and mispickel, is subjected to an oxidising roasting in a reverberatory furnace. Sulphur and arsenic are expelled in the form of sulphurous and arsenious acids, and the metals with which they were combined are converted into oxides. The arsenious acid is collected in long flues and condensing chambers, while the sulphurous acid is allowed to escape.

The dressed ore usually contains between 25 and 30 per cent. of tin.

If much arsenic be present in an ore, the greater portion of it is not removed in a single roasting; such ores must therefore be roasted more than once.

The chemical changes brought about by the oxidising roasting of a finely divided mass of tin ore, iron pyrites, copper pyrites, mispickel, bismuth and tungsten compounds—such as frequently forms the material for the extraction of tin—are as follows:—

The iron pyrites is partly converted into ferric oxide and partly into ferric sulphate, sulphurous acid being at the same time liberated. The ferric sulphate, as the temperature rises, is split up into ferric oxide and sulphur trioxide or sulphurous acid and oxygen. The sulphur trioxide acts on the sulphides, and also on the arsenides, which are still unchanged, oxidising them.

Copper pyrites is changed into a mixture of copper oxide and copper sulphate.

The tin ore remains unaltered, except a small portion which is changed into stannic sulphate.

Bismuth ores are converted into bismuth oxide.

Leucopyrite loses the greater part of its arsenic as arsenious acid; a small portion of the arsenious acid, however, is changed to arsenic acid and forms arseniate of iron with some of the iron.

Mispickel is converted into a mixture of ferric oxide, ferric sulphate and ferric arseniate, with disengagement of sulphurous and arsenious acids.

Tungsten compounds are unaltered.

The copper in the ore is, as far as possible, converted into copper sulphate, so that the latter may be extracted from the roasted charge by lixiviation.

As the result of the roasting there is obtained a mixture containing tin ore, oxides of iron, copper and bismuth, sulphates of copper and iron, a little tin sulphate, ferric arseniate, wolfram compounds, and small quantities of unaltered sulphides and arsenides.

Ferric arseniate is moderately stable at high temperatures; i order to decompose it, it is well to mix powdered coal or organic substances such as sawdust or pine needles with the charge. The iron is thereby converted into ferric oxide, while the arsenic acid is, by means of the carbon, converted into arsenious acid and suboxide of arsenic, carbon dioxide being produced.

Reverberatory furnaces for roasting are of two kinds: *a*, those in which the roasting chamber is fixed, and, *b*, those in which the whole or part of it is movable.

The latter are used in places where the cost of labour is high, or where the ores contain large quantities of sulphur and arsenic, and where there is a large quantity of ore to be handled. This is, for example, the case in Cornwall, where furnaces of the former kind have been almost entirely replaced by those of the latter. Most recently, furnaces with partly movable roasting chambers (the Brunton calciner) have given place to the more effective and capacious Oxland furnace, in which the whole chamber moves.

a. Furnaces with fixed Roasting Chambers

These possess either elliptical, rectangular or square beds, with only one working door in the short side opposite the fire. The length of the hearth varies from 7 feet 3 inches to 15 feet; the width (in elliptical beds the width of the widest part) is from 5 to 11 feet; the height of the roof above the bed is from 1 to 2 feet. The charge varies with the size of the furnace from ½ ton to 1 ton.

The arrangement of the furnace used in Saxony is shown in Figs. 278 and 279.

The ore is dried on the roof of the furnace and dropped into the roasting chamber through the opening *a*; *d* is the chimney; *c*, a flue by which the arsenious acid passes to the condensing chambers and towers. The chimney *d* can be completely shut off from the roasting chamber by the slide *b*; similarly the flue *c* can be shut off from the roasting chamber by a slide or a damper.

In roasting ores containing arsenic in this furnace, the slide *b* must, at the beginning, be closed, and the furnace strongly fired;

a great quantity of arsenious acid is given off by the ore, and this, as the chimney is closed, must pass into the condensing chambers. When the arsenious acid ceases to be given off, carbon is mixed with the charge to decompose the arseniates which have been formed, the opening into the flue leading to the condensing chambers is closed,

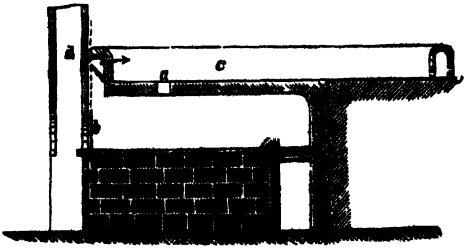

FIG. 278

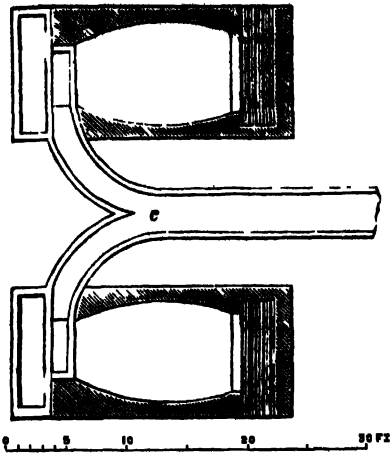

FIG. 279.

and that leading to the chimney is opened; the products of roasting then pass into the air.

If the ores contain very little or no arsenic, the gases from roasting and from the fire are allowed to pass at once to the chimney. With this kind of ore the furnace is at first gently fired, and the temperature gradually raised as the sulphur is driven out of the charge.

During the roasting, the charge must be regularly rabbled and turned from side to side, in order to bring each part of it continually into contact with the air, and also to prevent any fritting together.

A charge contains 12 to 15 cwt.; the time of roasting depends on the amount of arsenic in the ores; those which contain no arsenic will require from 6 to 8 hours, whilst those which do contain arsenic may require as much as 24 hours.

One or two workmen are required for each furnace. At Tostedt (Lüneburg Heath) furnaces with two working doors in the longer side are used. The charge contains from 16 cwt. to 1 ton. In 24 hours, from 16 cwt. to 2 tons of ore are roasted, according to the amount of sulphur present, the consumption of coal is 16 cwt., and one man on each shift is required for two furnaces.

At Par, in Cornwall, furnaces with elliptical hearths are used; the beds are 7 feet 3 inches long, 5 feet wide, and the height from bed to roof in the middle of the bed is 1 foot 4½ inches. The flues for condensing the arsenious acid, more than 300 feet long, are 6 feet 6 inches high and 3 feet 2 inches wide, and have cross-walls projecting alternately from each side; at the end of the flue is a high chimney. The charge consists of 10 to 12 cwts. and remains in the furnace 10 to 13 hours [illegible] a gentle red heat, being rabbled at intervals of 20 to 30 minutes. The coal consumption varies from 2 to 2·6 cwts.

Ores containing excessive quantities of arsenic are washed and subjected to a second roasting for 8 or 10 hours.

At Treleighwood, in Cornwall, the furnace bed is 10 feet square, and the fireplace 2 feet 6 inches square. One ton of ore there requires 3 cwts. of coal.

b. Furnaces with partly movable Roasting Chambers

Among furnaces of this kind must be mentioned the Brunton calciner which is used in Cornwall; the construction of it is shown in Figs. 280 and 281, in which *a* is the revolving bed carried by a vertical shaft. It consists of an iron frame, the upper surface of which forms an iron table fitted with concentric ridges; between these ridges are courses of fire-brick. The bed has the shape of a flat cone, the sides of which possess an inclination of ¾ inch to the foot. The diameter varies between 8 and 14 feet. In the furnace figured in the text it is 12 feet.

The vertical shaft, on which a large toothed wheel is keyed, is driven by means of the water wheel *A* through the cogwheels *k* and bevel gearing *i*. The bed makes 1½ revolutions in an hour.[1] The roof is 11 inches above the bed: *e* is the hopper through which the ore is fed, and which is fitted with an automatic arrangement for feeding. Above the bed are two or three fixed rakes with inclined tines 3 inches long, fixed in a frame. By the revolution of the table and the inclination of the prongs of the rakes, the ore is gradually worked from the centre to the edge of the table and landed finally at the discharge opening by the movable shoot *g*. Here it is, according to the position of the shoot, which is worked by the handle *l*, discharged alternately into one of the two chambers

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[1] Phillips' *Metallurgy*, p. 518. London, 1891.

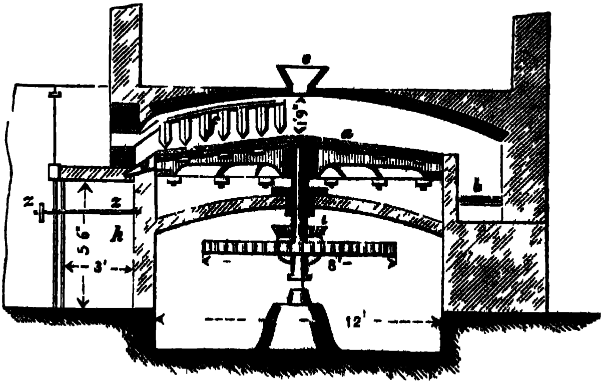

Fig 280

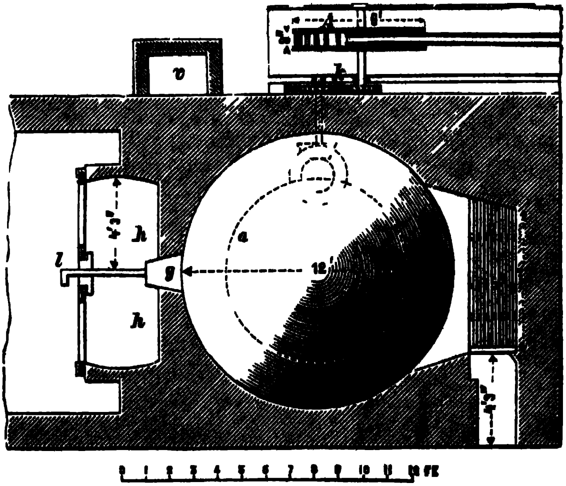

Fig 281.

h; the mouth of the chamber, while it is being emptied, is closed with a slide.

In a furnace of this sort 2 to 2½ tons of ore are roasted in 24 hours with a consumption of 2½ cwts. of coal per ton of roasted ore.

The washing of the roasted ore concentrates the tin to about 70 per cent., after which it can be roasted a second time at the rate of about 3 tons per 24 hours. The Brunton calciner has recently, in many works, been replaced by the revolving calciner of Oxland and Hocking.

Furnaces with movable Roasting Chamber

Of this kind of furnace that of Oxland and Hocking may be taken as a type. It is used in Cornwall, and has proved itself specially suited for roasting ores rich in sulphur and arsenic.

The arrangement adopted in English tin works is shown in Figs. 282 and 283.

B is the revolving cylinder from 30 to 40 feet long, and from 4 to 6 feet in diameter; it [illegible] built of boiler plate, lined with firebrick. As the ore travels forward by the turning of the cylinder, it meets four projecting longitudinal ridges of firebrick (see Vol. I, Fig. 64) between which it lies. The inclination of the cylinder depends on the nature of the ore to be roasted; with easily roasted ores it is greater than with those that require more time. The cylinder is provided with 3 bearing rings which work on friction rollers *c*. Motion is communicated to the cylinder by the action of the bevel wheel *Z* on the toothed wheel *D*, which is bolted to the shell.

The air which is necessary for oxidation enters the cylinder, warmed by its passage through the flue *i* in the roof *A* of the fireplace. The ore is fed into the upper end of the cylinder through the hopper *h* fitted with an automatic feeder. The longitudinal ridges, by the revolution of the cylinder, alternately raise and drop the ore when it reaches its angle of repose. Thus the ore is brought into repeated contact with the hot gases and air in the cylinder. Having arrived at the lower end of the cylinder, the ore falls through the opening *e* into the arched chamber *F*, from which it is removed through the door *f*. The cylinder makes from 3 to 8 revolutions per minute according to the nature of the ore.

The hot gases and vapours pass from the upper end of the cylinder into the system of condensing chambers *k*, *l*, *n*, *o*, *p*, in which the arsenious acid is deposited, and thence to the chimney. The deposit is removed through the openings *m*, *m*, which are built up during the working. The condensing chambers are covered with cast iron plates *g*, on which the ore is dried before roasting.

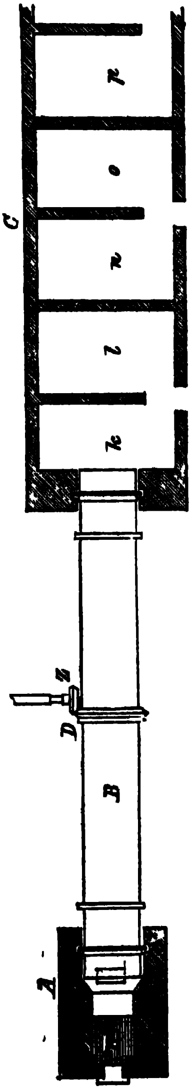

FIG 282

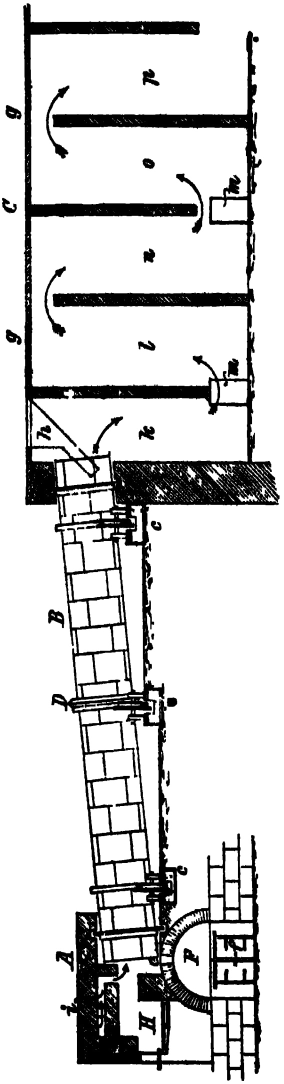

FIG. 283.

One man and a boy per shift of 8 hours are needed for the working of each furnace. The consumption of coal is considerably less, and the output considerably greater, than in the Brunton calciner; 20 to 25 tons of ore, according to the amount of sulphur and arsenic it contains, can be roasted in 24 hours with the consumption of 1 cwt. of coal per ton of ore.

Treatment of the Roasted Ore

After the ore is roasted for the first time, if it contain copper, it is washed with water, in order to extract the copper sulphate formed during the roasting, after which hydrochloric acid or dilute sulphuric acid is added to dissolve the copper oxide. From the washings the copper is precipitated by scrap iron. Oxides of iron and bismuth will also be dissolved by the hydrochloric acid.

At Altenberg, in Saxony, where the ores contain bismuth, the ore is allowed to remain in contact with hydrochloric acid for many hours in wooden tanks; after this, the solution of bismuth chloride which is obtained is diluted with water in a second set of tanks in order to precipitate basic chloride of bismuth. The liquor is then run off into a row of vats where the basic chloride settles down, the solution is separated from the precipitate, and the latter dried and smelted in graphite crucibles with lime and charcoal.

Removal of Tungsten from the Roasted Ore

The wolfram, which cannot be removed either by dressing nor by extraction with acids nor by roasting, used to be extracted at the Drakewells Mine by fusing the roasted and washed ore with soda ash. This process, due to Oxland, depends upon the conversion of wolfram into sodium tungstate which is soluble in water. The process was carried out in a reverberatory furnace, the hearth of which consisted of a shallow cast-iron pan.

The construction of this furnace is shown in Fig. 284; *a* is the cast-iron pan into which the charge is introduced through the opening *z* in the roof; *b* is the fireplace. The flame passes first over the pan and firebridge *g*, then down the vertical flue *f* and along under the pan, finally issuing to the chimney *i*, through the flue *e*. The quantity charged at one time varied from 10 to 11 cwt.; with coarse ore, a greater quantity was charged at one time.

The ore was first charged and the soda ash added as soon as it had attained an incipient red heat. The mass was then well rabbled and brought up to a bright red heat. The quantity of soda ash added was such that a small excess was present beyond that which was needed for the formation of sodium tungstate. In working this process the charge must not be allowed to melt, the particles of tin ore being kept unfused. The charge remains 2½ to 3 hours in the furnace, after which a portion only of it is drawn off through an opening in the bed (not shown in the figure), into an arched chamber underneath. In 24 hours, 3 to 4 tons of ore can be worked with a consumption of 6 cwt. of coal. The fused mass is placed while still hot in lixiviating tanks and there treated with water; the solution obtained is evaporated either to the strength at which it will crystallise, or to dryness; in the latter case the residue will contain 70 per cent. of sodium tungstate.

The residue from the lixiviation is washed till the oxides of iron and manganese, formed by the decomposition of the wolfram, are completely removed.

This method has been given up, or is only rarely used; it is expensive, and there is some loss of tin, consequent on the formation of stannates; and further, the market for tungsten compounds is limited, and their price is low.

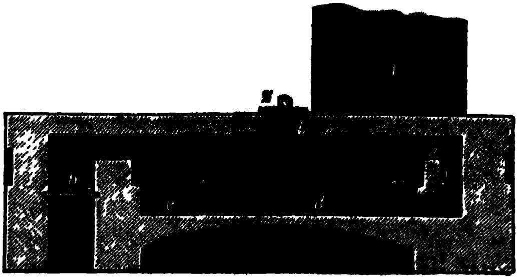

FIG. 284.

Glauber salt, or sulphate of soda, being cheaper than soda ash, is used in place of it, coal being added to decompose the sulphuric acid. The furnace is first worked with a reducing flame, which with the coal present in the charge reduces the sulphuric acid of the glauber salt to sulphurous acid which escapes; the furnace is then worked with an oxidizing flame by which the wolfram is converted into sodium tungstate and oxides of iron and manganese.

The charge is 9 cwts., and 4 charges are worked in 24 hours. The mass is lixiviated, while still hot, in tanks filled with water. Both solution and residue are treated in the same way as in the soda ash method. This process, which demands great care, has, on the above-mentioned grounds, also been given up.

A method has been proposed by Michell for treating ores which contain at the same time copper and wolfram. The ore is subjected to a chloridising roasting with common salt, by which the wolfram is converted into sodium tungstate, and the copper to copper chloride; arsenic, antimony and bismuth, if present, will be volatilised as chlorides. From the solution which will contain the copper and tungsten, the former can be precipitated with iron, and the latter by calcium chloride as calcium tungstate. This practice has also been given up, though it was for a time used in Bohemia and Cornwall.

At present the most practical way is to separate the wolfram from tin ores by hand picking.

Ore which has been once roasted and washed, if it is free from sulphides and arsenides, or if it contain very small quantities of these, is smelted for the production of tin. If, however, it contains considerable quantities of these impurities, as is usually the case in Cornwall, it is subjected to another roasting and washing for the removal of the last portions of the sulphur and arsenic, and of the oxide of iron formed in the roasting. This second roasting and washing would be performed in the same plant as the former ones, and the ore, after this treatment, would be smelted to produce tin.

In Bohemia, Saxony, and some English works, ores are only once washed and dressed. The dressing of the roasted ores is done in Cornwall by round buddles and kieves, and occasionally, as at Abertham, near Bärringen, in Bohemia, in centrifugal jigs.

2. THE REDUCTION OF TIN ORE

The reduction of tin ore is effected by smelting it with carbon. In this process only just enough slag must be formed to protect the reduced tin from oxidation by the air, unless additions are required to keep the charge open, or unless considerable quantities of impurities have to be removed. The reason for this is that tin oxide has the power to act either as a base or as an acid, and, consequently, is very easily carried into the slag. The tin oxide which is carried into the slag can be reduced to metal by employing a sufficiently high temperature; but the latter is always contaminated by other metals reduced at the same time from their oxides in the slag. This is especially the case with iron (and copper, if it be present). Further, shots of tin, or *prill*, always become entangled in the slag.

The first principle of the reduction of tin ore, therefore, is to keep the quantity of slag as small as practicable. This renders it necessary that the ore should be concentrated as far as possible before smelting by the preliminary treatment (dressing, roasting, lixiviation). If tungsten minerals remain in the ore when it is smelted, part of the tungsten goes into the tin and part into the slag, making it less easily fusible.

The reduction process can be carried out in a shaft furnace or in a reverberatory furnace.

Shaft furnaces are only used where charcoal can be obtained at a low price. Coke would cause the formation of a greater proportion of slag, on account of its high percentage of ash, all of which would have to be converted into slag; it is therefore not used. If the ore is in the form of powder, as is usually the case, as the result of the previous dressing, some material must be added to the charge to loosen it, and slags are chosen for this purpose; this causes a still further increase in the amount of slag produced, and a corresponding rise in the quantity of tin which is slagged away.

Tin produced in shaft furnaces is less pure than that produced in reverberatory furnaces, because of the more perfect reduction which takes place in the former.

It is possible in the shaft furnace to remove volatile impurities more completely than in the reverberatory furnace, but the loss of tin by volatilisation is greater than in the reverberatory furnace. In order to prevent as far as practicable the reduction of foreign metallic oxides, and the admixture of the corresponding metals with the tin, shaft furnaces should be comparatively low; this, however, reduces the output of the furnace. Also, for the reasons given above, the temperature at the tuyeres must be kept as low as practicable, and therefore it is not possible to increase the production of the furnace by heating the blast; further, the tin, on account of the ease with which it is oxidised, must be removed as soon as possible from the stream of air entering the furnace.

The reverberatory furnace needs no addition of any material to charges of fine ore for the purpose of loosening it; it allows the use of solid crude fuel, as well as of gaseous and liquid fuels; it is capable of a greater output than the shaft furnace, and permits the production of a purer tin, on account of the less severe conditions of reduction.

This form of furnace requires that carbon be mixed with the ore as a reducing agent. A non-caking coal is the reducing agent usually adopted, and if it contain a small percentage of ash, a smaller proportion of slag is produced than in shaft furnaces. In the same way there is a smaller loss of tin through volatilisation.

The disadvantages of the reverberatory furnace are that the bed retains a proportionately greater quantity of tin, which can only be recovered at the end of a campaign, and that the slags are richer in tin. In spite of these, however, tin ores are preferably reduced in reverberatory furnaces. Shaft furnaces are only used where it is possible to get charcoal at a low price, and where coal is at the same time dear, and where small quantities of coarse-grained ore have to be smelted. At the present time, therefore, the use of reverberatory furnaces is on the increase. Shaft furnaces, which in the past were widely used, are now only to be found in the places where the above conditions exist.

a. The Reduction of Tin Ore in Reverberatory Furnaces

Reverberatory furnaces are used for the smelting of tin ore in England, Australia, France, Tasmania, California, Singapore, and have been introduced recently into Germany, at Tostedt, near Hamburg.

The furnace consists of an elliptical bed, built of fire-clay, from 4 feet 6 inches to 12 feet in length, and from 3 feet 3 inches to 8 feet in greatest width. The length most usual at present in England is 12 feet, and the width at the widest part, 8 feet. At Villeder, in France, the length of bed is 11 feet, the width 6 feet 6 inches, and the mean height of the roof above the bed, 12 inches. Smaller furnaces have the following dimensions:—length of bed, 4 feet 6 inches; width of bed at the widest part, 3 feet 4 inches; width at the fire-bridge, 2 feet 4½ inches; width at the end, where the flame leaves the bed and enters the flue, 1 foot 3 inches.

These furnaces have two working doors—one in the short side opposite the fire, and one in the long side at the back of the furnace; in the front of the furnace is the taphole, and below it is the pot to receive the metal.

The construction of a small furnace, with a bed of 4 feet 6 inches in length, and 3 feet 3 inches in width, is shown in Figs. 285 and 286; *e* is the bed, *b* the working door at which the ore is charged, *o* the working door at which the slag is drawn. The bed is supported by a grid of iron bars, under which is the *vault h*, which serves to keep the bed cool; *d* is the firegrate with the fire-door, *c*; *g* is the fire-bridge, through which a channel is built to keep it cool; *f* is the opening by which the flame leaves the furnace; *n* is the flue and *m* the chimney; *i* is a subsidiary stack connected with the fire-place by the opening, *a*, in the roof, into which the products of combustion are led while the furnace is being charged, in order to prevent the fine ore being drawn into the chimney, *k* is the taphole, which is connected on the outside of the furnace with the kettles, *l*, *l*, for receiving the metal.

The construction of a larger furnace is shown in Figs. 287 and 288[1]; the bed of this one is 12 feet in length and 8 feet in width. *A* is the bed, *B* the charging door, *E* the door for drawing the slag, *C* the fire-grate with fire-door *D*. *G* is the kettle or float for receiving the tin, and *H* is a cast-iron kettle, heated by a separate fire underneath, which serves to receive the metal when the crude tin is refined by liquation in the same furnace; it is also used to contain the liquated metal while it is being *boiled*. *N* is the stack, built and bound in with the furnace, and connected with it by an

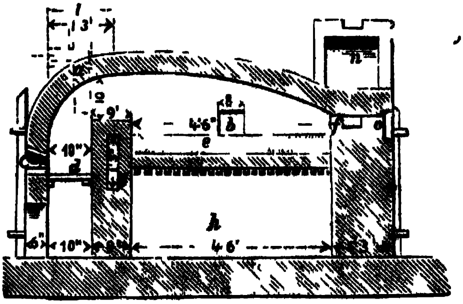

FIG 285

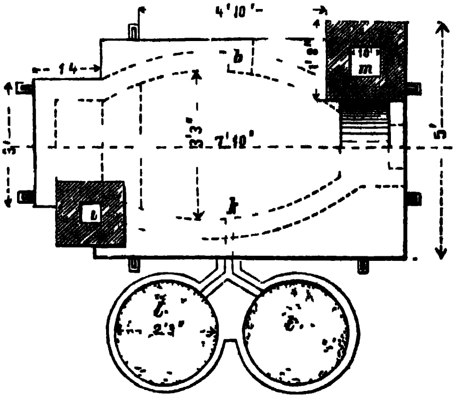

FIG 286.

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[1] For drawings of the most recent form of Cornish furnace, see also H. Louis, "The Metallurgy of Tin." *The Mineral Industry*, 1896, vol. v. p. 533.

inclined flue. The kettle for receiving the metal when the furnace is tapped is lined with fire-clay. The weight of the charge of ore for this pattern of furnace varies, according to its size, and the richness of the ore, between 15 cwt. and 4 tons.

The ore before it is charged into the furnace is mixed with one-fifth of its weight of non-caking coal or anthracite, as low as possible in ash, and sometimes with a small quantity of lime or fluorspar to flux the constituents of the ash of the coal. The mixture is wetted to prevent the dust being carried away during charging, and thrown on the bed through the charging door, after which it is levelled from both working doors.

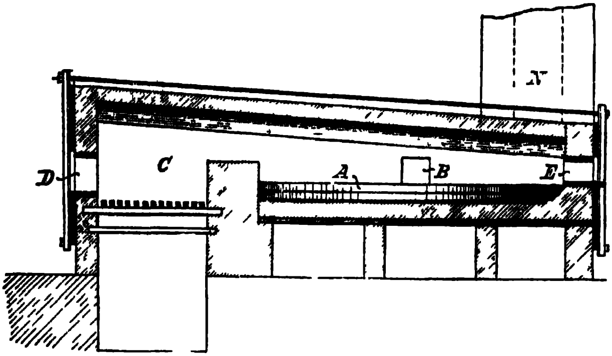

FIG 267.

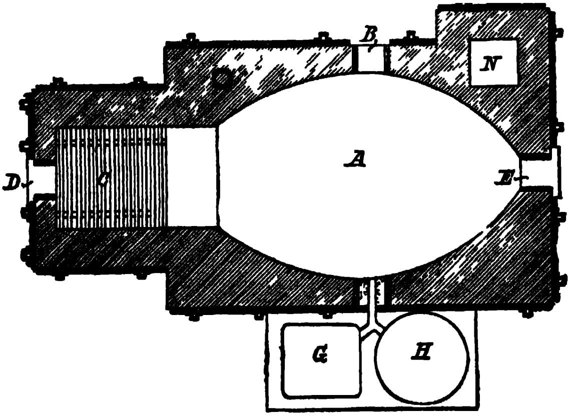

FIG 268

The normal working of a charge, which according to its size remains from 6 to 12 hours in the furnace, is as follows:—First, all doors being shut, a regular fire is applied during from 5 to 8 hours. At the end of this time, the fused mass is thoroughly stirred, this being done through the slag door, the position of which under the chimney prevents the stream of air which rushes in from coming in contact with, and oxidising, the tin. After this a strong heat is applied for a further period of from ¾ to 1 hour, and the charge is again stirred. The reduction of the tin, as well as its separation from the slag, should now be complete. The slag is now either skimmed off from the metal through the slag door, after being stiffened by the addition of fine coal, and the tin is run out with a small quantity of slag; or else both slag and metal are tapped together In the latter case the slag is allowed to "set" on top of the metal in the pot, and then lifted off. The tin is now either cast into ingots or passed on in the liquid state to be refined. A spongy mass of slag remains on the bed after tapping: this retains mechanically a considerable quantity of tin prill; it is drawn through the slag door, after which the furnace is again charged.

The whole process lasts from 6 to 12 hours according to the size of the charge and the quality of the ore and fuel. In Cornwall 7 hours are required to work a charge of 22 cwt.; in France one of 1½ tons is worked in 6 hours; and in Australia 1 ton is smelted in 12 hours.

The coal consumed varies from 66 to 120 per cent. of the ore smelted, when it is rich (65—75 per cent. tin); for poorer ores and larger furnaces 50 per cent. of coal is enough. From 1 to 3 workmen on each shift are required to work a furnace. The loss of tin in smelting is from 5 to 7 per cent.[1]

The products of this process are tin and slag. The tin, if derived from a pure ore, will be at once taken in the fluid state to be refined either in the boiling kettle or in a special refining furnace; if it be impure it will be cast into ingots and subjected to liquation. The slags are silicates of tin and of the other metallic oxides contained in the ore; they also contain tungstic acid if wolfram be present in the ore. Their constitution varies; in most cases they are mixtures of mono- and bi-silicates, and contain mechanically enclosed prill as well as oxide of tin.

The following analysis gives the composition of ore slag examined by Berthier; it had been run in a reverberatory furnace at

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[1] *Engineering and Mining Journal*, 1892, vol. 54, No. 1, p. 3.

Poullaouen, in France, from an ore from Piriac, and dressed tin dross :—

SiO_2	40·0	per cent.
SnO_2	8·4	"
FeO	20·3	"
MnO	11·1	"
CaO	3·6	"
MgO	1·0	"
Al_2O_3	9·6	"
	94·0	

Three sorts of slags are usually distinguished, viz. :—

(1) Poor slags which can be thrown away. (2) Richer slags (5 per cent. tin) containing mechanically enclosed prill, from which the richer portions can be separated by a dressing process, to be afterwards smelted up with tin produced by smelting slag: and (3) the slag remaining on the bed after tapping, which contains a large quantity of prill; this can be treated by smelting it with tin ore or with the rich product obtained by dressing the above mentioned second kind.

In Cornwall, ores which have been concentrated from 2 per cent. to 65 or 70 per cent. by dressing and containing 4 to 5 per cent. of iron, are mixed with one-fifth of their weight of anthracite into charges of 22 to 24 cwts. and smelted in 7 hours in furnaces of the larger pattern, shown in Figs. 287 and 288. It is only rarely that fluorspar, lime or common salt is added as a flux in the case of difficultly fusible ores. 100 parts of ore in a state of fine division called *slimes* require 110 to 120 parts of coal, exclusive of that used as a reducing agent, and produce 60 parts of crude tin with a loss in smelting of 6·5 per cent.

In Australia (Sydney and Brisbane) ores of 69 to 70 per cent. are invariably smelted with Australian coal in charges of 1 ton; 12 hours is required for a charge. At Mount Bischoff the ores are dressed up to 47 or 48 per cent. and are smelted at Launceston in small reverberatory furnaces. The loss of tin is 4·27 per cent. and the fine metal obtained contains 99·85 per cent. Sn.

At Villeder, in France, where the furnaces are 11 feet in length on the bed, with a width at the widest part of 6 feet 6 inches, the charge consisted of 1½ ton of ore and 6 cwt. of anthracite, and is smelted in 8 hours. In 24 hours, 6 tons of ore are worked with a consumption of 9 tons of coal, exclusive of the anthracite mixed with the charge; 1 workman manages each furnace.

At San Jacinto,[1] in California, crude petroleum was used, being a cheaper fuel at this place than coal would be.

At the Tostedt Works on Lüneburg Heath (Kreis Haarburg), in 1895, Bolivian, Spanish and African ores, varying in richness from 40 to 74 per cent. were smelted in Cornish furnaces, after a preliminary roasting: there are 2 smelting furnaces, 1 small one and 1 of the largest size. In the small furnace the charge is 30 to 36 cwts. of roasted ore, and in 24 hours 72 cwts. are smelted with a coal consumption of 48 cwts.; each shift consists of 2 men. The larger furnace which needs a gang of 3 men on each shift, takes a charge of 3 to 4 tons; in 24 hours 132 cwts. of ore are treated with a consumption of 64 cwts. of coal. The slag produced from ore smelting contains 20 to 25 per cent. of tin and is re-smelted in the same furnaces. In the smaller furnace with a gang of 2 men, 90 cwts. of slag are smelted, 44 cwts. of coal being consumed: in the larger furnace, with a gang of 3 men 180 cwts. of slag are treated in 24 hours, 60 cwts. of coal being required. The slag produced from this second process is again smelted 2 or 3 times in shaft furnaces for the recovery of the tin it contains.

Smelting in Reverberatory Furnaces in the Straits Settlements

In general outline, the process is a development of the Australian one; Australian smelters having been employed to work out a method which was adapted to the conditions prevailing in the Straits Settlements.

The furnace employed is larger than those usually found in tin works: the charge of ore is 4 tons, and the size of bed 16 feet × 9 feet. Charges of 6 tons have been worked, but this was only possible in a gas regenerative furnace, in which the working was not satisfactory.[2]

An important and novel feature of the Straits furnace is the "water-vault." In ordinary furnaces the leakage of tin through the bed into the vault is considerable, even when the utmost care is taken to secure a tight job, and the melted metal has constantly to be ladled out of the vault. Some, however, always penetrates into the foundations, below the floor of the vault, and into the ground still further down; it travels onward and downward under the fluid pressure, which is considerable, as long as the ground has a temperature above the melting point of tin, 260° C. The brick-

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[1] *Engineering and Mining Journal*, 1892, vol. 54, No. 1, p. 3.

[2] McKillop and Ellis, *Inst. Civil Eng.*; 1895–1896.

[illegible] and concrete of a furnace and the ground on which it is built are constantly at a temperature of 260° C. or more for several feet from the furnace walls, and hot tin can only have the effect of still further raising the temperature of the ground into which it percolates.

The amount of tin which accumulates in and under a furnace which has been working for some time is very great, and as it can only be recovered when the furnace is demolished, the charge for interest is heavy.

The water-vault furnace[1] completely obviates these difficulties. The vault is deeper than in the ordinary furnace, and consists of a water-tight tank extending under the whole area of the bed and fire-bridge, so that all leakage shall drop into it. It is filled with water to a depth of at least 6 feet, and the result is that tin droppings are at once cooled and retained in the vault. At the end of a week or fortnight the water is pumped out and the granulated tin recovered. If care be taken to maintain a sufficient depth of water in the vault, no explosion can occur, as any red-hot charge falling into the water is quenched. Danger exists when there is insufficient water; in this case when a red-hot charge falls into the vault, instead of merely raising the temperature of a large body of water, it converts the smaller quantity into steam with explosion; 8 feet of water has been found sufficient in practice.

The variations in practice in the Straits Settlements are such that the slag from smelting ore is moderately rich in tin, while the metal is very pure. The ore slag is smelted with culm and sufficient iron to displace all the tin from the silicate of tin ("glass-slag") formed in the first process. The result is a clean and poor slag, which can be thrown away, and a metal containing considerable quantities of iron. The latter is removed by liquation and refining, and is used for decomposing fresh charges of slag (silicate of tin).[2]

b. The Reduction of Tin Ore in Shaft Furnaces

The extraction of tin in these furnaces is practised in Saxony, Bohemia, Bolivia; Billiton, Banca and the Malay Peninsula, and other parts of the Far East.

Shaft furnaces must be low because otherwise foreign oxides would be reduced and their metals would alloy with the tin; *sows* would also be formed in the furnace. They are, therefore, not built more than 10 feet in height. As the reduction of the ore demands a high temperature, the shaft is contracted at the zone of fusion.

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[1] McKillop and Ellis, *loc. cit.*

[2] See Louis, *The Mineral Industry*, vol. v. 1896.

The width of the mouth is [illegible] 2 [illegible], and the depth (from back to front) from [illegible] feet to [illegible] feet [illegible] inches.

In order that the tin may get away as quickly as possible from the oxidising action of the blast, and to prevent the formation of *sows* on the sole-block, these furnaces are always built on the "*spür*" principle,[1] and are usually worked with an open tap-hole or *eye*. They are provided with dust chambers to collect the volatilised tin and the fine ore which is carried away by the blast.

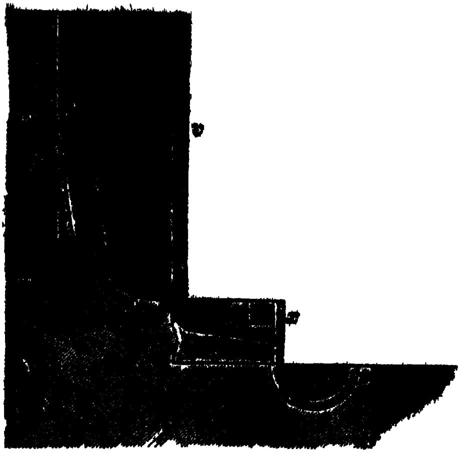

FIG. 289

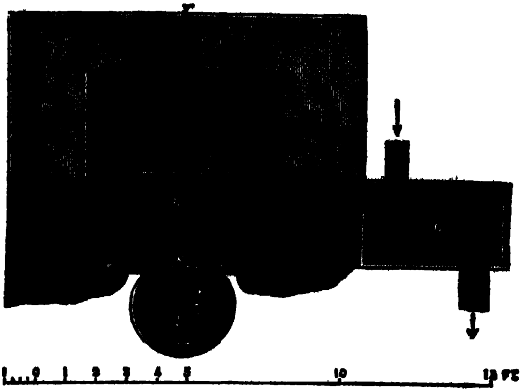

FIG. 290

The construction of a furnace at Altenberg, in Saxony, is shown in Figs. 289 and 290.

In these *k* is the inner lining of granite 10 feet 2 inches high, which is enclosed on three sides by the granite or gneiss outer wall *r*; *v* is the front wall. The sole block *o* is formed by a granite slab inclined at an angle of 26°, and well covered over with a brasque of fire-clay containing a small proportion of coal dust. The furnace cavity which diminishes in area from above downwards is trapezoidal in horizontal section. The blast enters through two tuyeres in the back wall of the furnace.

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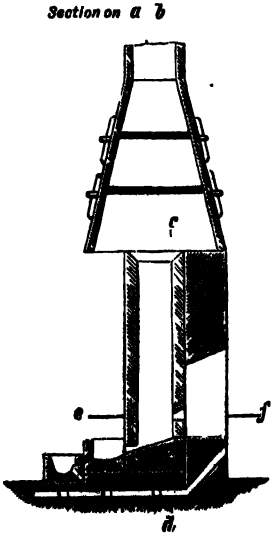
[1] *i.e.* with an arrangement by which the tin collects in a pot (*vortiegel*) outside of the chamber in which the reduction takes place. See vol i. p. 93.

The fused products pass through the open *eye* of the furnace into the *vortiegel* *w*, hollowed out of a slab of brasque which forms the fore-hearth of the furnace. Here the tin and slag separate from each other; the slag is allowed to flow over the slag-notch and over an iron plate *u* connected with it, into the tank *g*. The latter is filled with water, and by means of supply and discharge pipes can be kept at a fixed temperature. The slag, which contains tin mechanically enclosed, is chilled in the water, and is thereby brought into a suitable state for subsequent crushing. The tin is tapped through the taphole *z* from the *vortiegel* into the tapping pot (*stechherd*) *s*; the taphole is 3½ inches wide, and passes through the iron plate *x*, which is 4½ inches thick. The *stechherd* is made of either cast-iron or granite, with a lining of clay, and is 1 foot 7 inches in diameter and 1 feet 4 inches deep. Beyond the furnace is a system of dust chambers not shown in the figure.



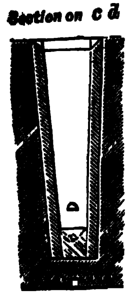


FIG. 292.

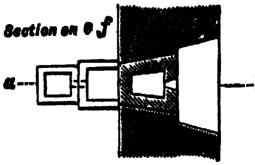


FIG. 291.

FIG. 293.

The construction of a furnace at Graupen, in Bohemia, is shown in Figs. 291, 292 and 293.

One tuyere only is used, and the shaft is 8 feet 10½ inches high and trapezoidal in horizontal section. The sectional area of the cavity is diminished from above downwards by the convergence of the side walls. The lengths of the parallel walls at the mouth are:—the front 1 foot 6 inches and the back 1 foot 8 inches: at the tuyere level the lengths are:—the front 10 inches, the back 13½ inches. The inclined sole-block is formed of a fine grained sandstone; formerly porphyry was used for this purpose. The inner lining is built of a fire-resisting stone.

In Banca, three-tuyere furnaces are used (Vlandeeren's furnace). They are worked on the *spiir* principle, and are square in section internally. They are 9 feet 2 inches in height, and the blast is supplied by a fan: the construction of one is shown in Figs. 294 and 295.[1]

A is the shaft, *B* the open eye (taphole) of the furnace, *C* is the *spiirtiegel* (cavity in which the runnings collect), *E*, *E* are the tuyeres, *D* is the fan. These furnaces have replaced the older Chinese furnace with advantage. The smelted tin is ladled out of the *spiirtiegel* into iron moulds and sent to market, the hard tin [$FeSn_2$] which remains behind (in the *spiirtiegel*) being first liquated.

In the Malay Peninsula shaft furnaces are also used. They have, however, very largely gone out of use at the present time, especially as regards the older Chinese furnace[2] built of wooden stakes and clay. The dressed ores are now in part smelted in reverberatory furnaces. The older Chinese furnace was built as follows:—wooden stakes 8 feet long were fixed in the ground close together, so as to form an inverted truncated cone 6 feet 6 inches high, with a diameter at the top of 5 feet, and at the bottom of 3 feet 4 inches. They were then bound together with flat bands of rattan, and the whole of the interior of the cone filled with clay well rammed together; in this the furnace cavity proper was then hollowed out. This cavity was 5 feet deep and had a diameter at the top of 1 foot 6 inches, and at the bottom of 10 inches. The opening by which the blast was admitted was placed 3½ inches above the lowest point of the cavity. The primitive blower was made out of a hollowed tree trunk, with 2 air exits and clack valves, and a piston which was moved backwards and forwards[3] by a coolie.

The shaft furnaces in the larger works in the state of Perak in the Malay Peninsula are built of brick with an outer wall of rough masonry, and are worked on the *spiir* principle with open *eye*. They are 6 feet 6 inches high from the level of the floor. The cavity is semi-circular in cross section and has a diameter at the top of 1 foot 6 inches, which diminishes to 6 inches at the *eye*.

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[1] *Jaarboeck van het Mijnwezen in Neederlandsch Oost-Indie*, 1872.

[2] For full descriptions of the Chinese methods of smelting, see H. Louis, "The Metallurgy of Tin." *The Mineral Industry*, 1896, vol. v. pp. 544 *et seq.*

[3] Cramer, *Oesterr. Zeitschr.* 1894, p. 543.

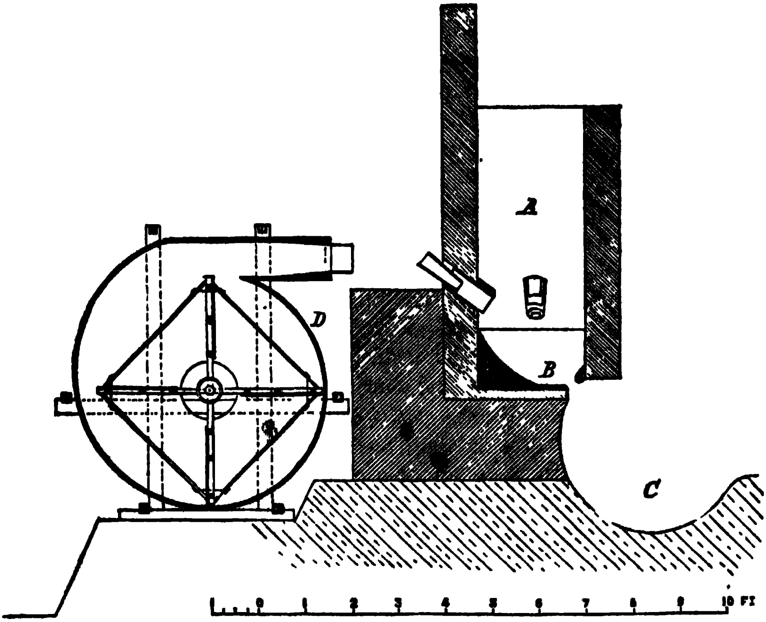

FIG. 294.

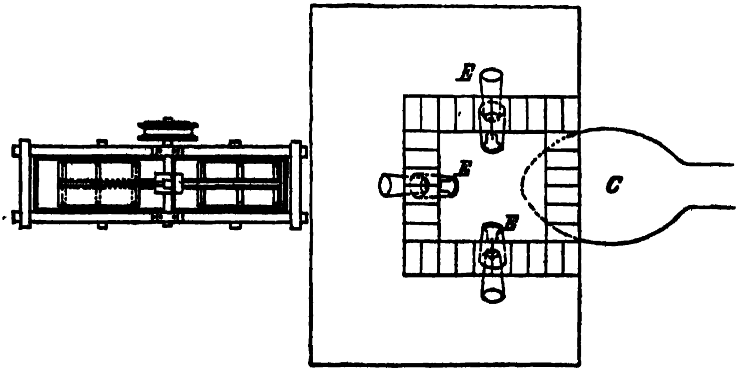

FIG. 295.

The construction of a furnace of this kind can be seen from Figs. 296 and 297. It has only one opening for the admission of the blast, which is produced in the primitive manner described above in connection with the older form of Chinese furnace. *A* is the outer casing, *B* the cavity, *C* the *eye*, *D* the forehearth, *F* the tuyere inclined at an angle of 40° or 45°, *G* the blower, *E E* are stages leading

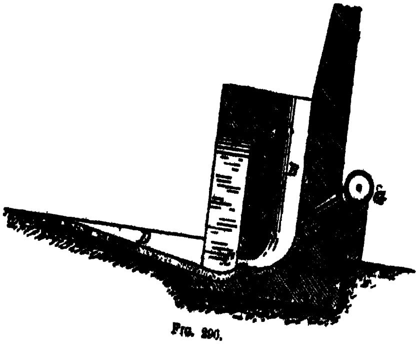

Fig. 296.

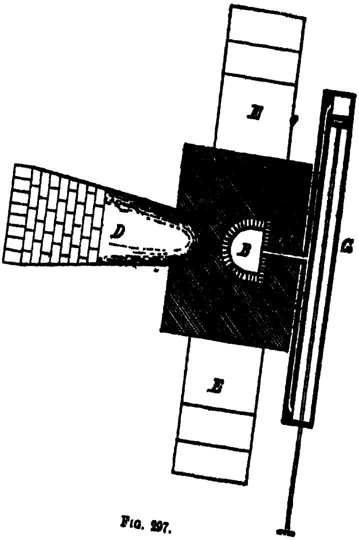

Fig. 297.

up to the mouth of the furnace. The blower requires the services of 3 coolies.

The ore is mixed with slags from a similar previous process and dross, the slag which is added serving as a loosening material and as a flux. A basic iron slag could not be used for this purpose because of the slagging of tin and reduction of iron, and consequent formation of *sows* or *bears* which would result. The foreign constituents of the ore pass chiefly into the slag, but part of the metals reduced from them, especially iron and copper, alloy with the tin. If the ores contain wolfram, part of tungsten is found in the slag, and part in the tin. In this case the slag will be less fusible.

Tin and slag together run from the furnace into the forehearth and arrange themselves according to their densities; if the tin contain iron, a difficultly fusible alloy of tin and iron, the so-called *hardhead* frequently separates out in the forehearth. The slag is either lifted off the tin, or allowed to run over the slag-notch (generally into a tank containing water). The tin is usually tapped from the forehearth into a tapping pot placed in front of it.

The amount of slag added to the ore may be as much as 50 per cent.; the total quantity worked depends on the size of the furnace, and amounts to upwards of 3 tons in 12 hours; 32 cwts. of ore containing from 50 to 60 per cent. of tin will require nearly 7·6 cubic yards of wood charcoal. One or two labourers are required for each furnace. The loss of tin is 15 per cent., of which from 8 to 9 per cent. is carried away by volatilisation. The products are crude tin, slag and the so-called hardhead.

The crude tin from the blast furnace is not yet pure and must be refined. Its composition, according to an analysis by von Lill of a sample from the Schlaggenwald in Bohemia is:—

Sn	97·339 per cent.
Fe	0·684 „ „
Cu	2·726 „ „
As	trace
S	trace
	100·749

The slags are silicates of the metallic oxides contained in the ores, particularly ferrous, manganous and aluminous oxides with small quantities of silicates of lime and magnesia. They also contain tin oxide, partly combined with bases, partly with silica, and partly as undecomposed oxide mechanically held by the slag. When wolfram is present in the ore, the slags will contain also tungstates of iron and manganese. They are, according to the proportion of silica which they contain, a complicated mixture of mono- and bi-silicates with variable quantities of compounds of stannic and tungstic acids; and they always contain considerable amounts of metallic tin partly in a state of fine division and partly in the state of coarse prill.

The composition of these slags can be seen from the two following analyses of specimens from Altenberg:—

	I. Lampadius. Per cent.	II. Berthier. Per cent.
SiO_2	20·05	16·0
SnO_2	25·12	32·0
WO_3	—	1·0
FeO	30·15	41·0
MnO	—	1·7
CaO	1·10	3·7
MgO	1·23	1·7
Al_2O_3	5·0	2·4
	82·65	99·5

The slag is subjected to repeated smeltings with charcoal in shaft furnaces in order to extract the tin it contains. The first time this is done (the so-called *schlackenverandern*), it produces slag-tin (*schlackenzinn*), and a slag which contains mechanically a large quantity of metallic tin. This slag is smelted again and yields *schlackenzinn*, and a second slag which still retains metal mechanically. These latter slags, as well as slags rich in tin from the preceding processes, are subjected to a process of dressing, in order to get a product rich in tin, which can be added to slag- or ore-charges; at the same time the refuses obtained in smelting and refining, such as liquation dross, hardhead, skimmings, furnace dross and flue dust, are worked up.

The smelting of slags is done either in ore furnaces, following immediately upon the ore smelting, or in special shaft furnaces of small height to prevent the reduction of ferrous oxide.

It frequently happens in smelting ores containing iron, and more so in smelting slags, that tin-iron alloys (hardhead) are formed, which deposit in the forehearth. These alloys, which have a grey or white colour and a crystalline structure, and are very brittle, are formed in consequence of the property of tin of uniting in all proportions with iron to form a series of alloys of very similar properties. Alloys of this kind, possessing the formula Fe_4Sn (Berthier), FeSn (Deville and Caron), and $FeSn_2$ (Nöllner) have been isolated.

The composition of hardhead from Altenberg in Saxony will be seen from the following analyses:—

	Fe_4Sn.			$FeSn_2$.
	I. Lampadius. Per cent.	II. Berzelius. Per cent.	III. Berthier. Per cent.	IV. Plattner. Per cent.
Sn	30·5	31·4	32·22	80·89
Fe	61·5	62·6	64·14	17·16
W	0·9	1·6	1·64	—
As	1·45	—	—	—
Cu	—	—	—	0·99
Carbon	0·95	—	—	0·96
Slag	3·51	2·4	—	—
	98·81	98·0	98·00	100·00

Hardhead is smelted with the other refuse products of tin extraction.

Examples of Shaft Furnace Practice

The tin-bearing rock mined in Altenberg and Zinnwald in Saxony, called *zinnzwitter*, is concentrated by dressing and roasting from ½ per cent. up to 50 or 60 per cent. of tin, and is smelted with wood charcoal in the above described furnace with the addition of from 25 to 50 per cent. of slag from a previous similar process, 6 or 7 per cent. of dressed furnace dross and variable quantities of washed drosses and hardhead.

The furnace is worked without a *nose* on the tuyere.

Tin and slag collect in the forehearth whence the slag is allowed to flow into a tank containing water, while the tin is tapped at intervals of 8 to 12 hours into the tapping pot; if the tin remains longer in the forehearth, hardhead separates out there.

When the furnace is working properly, the tin which runs from the furnace should be red-hot, and the charcoal visible through the tuyere hole should be at a yellow heat; if, however, the temperature rise too high, both the fuel visible through the peephole, and the issuing tin will be at a white heat.

In 24 hours, 32 cwts. of ore and 16 cwts. of slag can be worked; from 7·2 to 7·8 cubic yards of charcoal are used for every 2 cwts. of tin produced. The loss of tin amounts to 12 or 15 per cent., of which 8 or 9 per cent. are due to volatilisation. The campaign lasts only 3 or 4 days. After the ore smelting, it is usual to follow on immediately in the same furnace with the treatment of rich slags and other intermediate products.

The slags contain unaltered tin ore as well as tin in the form of prill. This treatment yields slag-tin (*schlackenzinn*) and so-called "*veränderte*" slags containing still large quantities of tin. These are subjected to a further smelting (the so-called "*schlackentreiben*") in shaft furnaces.

The products of the ore smelting are crude tin, slag and hardhead. The crude tin is refined (either by *boiling* or by liquating), the slags are further smelted to extract the tin they contain, and the hardhead, after a preliminary calcination, is added to the charge in the *verändern*.

At Graupen, in Bohemia,[1] ore is extracted from gneiss which carries from ½ to 10 per cent. with an average of 2 per cent. When this is dressed it yields coarse concentrates, tin ore containing from 68 to 72 per cent. of tin, and slimes (*schliche*) with from 45 to 48 per cent. These are smelted in conjunction with ores from Bolivia, except when tin of special purity is required, in which case the concentrated ores are smelted by themselves. Ores which contain bismuth are previously roasted and treated with hydrochloric acid for the extraction of that metal.

The smelting of these ores is effected in the furnaces described and figured above, which are worked with a dark top and without *nose*. Slags are added to the charge as a flux. After tapping, the tin is skimmed in the tapping pot and cast into bars. The slag which flows into the forehearth with the tin is from time to time lifted off and thrown into water. If the temperature rises too high, wet charcoal is used. In 24 hours, 22 to 24 cwts. of ore are smelted, using 13 cubic yards of charcoal. The slags contain 10 per cent. of tin.

The first smelting (*verändern*) of the slag, which is previously reduced to the size of peas, follows on the smelting of a run of ore. In this process a higher pressure of blast is used and the diameter of the taphole is increased from 1½ inches to 3 inches. Further, on account of the greater fluidity of the slag from this operation, the tin is ladled from the forehearth; if it were tapped into the *stechherd*, the slag would run with it and would stop up the taphole. The slag obtained is quenched in water, crushed and smelted in the same furnace after the slag obtained from ore-smelting is finished. This second smelting of slag is called the *treiben*. The products are tin and a twice smelted slag which still contains tin mechanically enclosed in it; it is therefore stamped and washed, the portions rich in tin being added to the charges in a subsequent smelting of ore or slag. Furnace residues (old bricks, &c., containing tin) are also stamped and washed.

In Banca the ore is first dressed and then smelted in the threetuyered furnace, 9 feet 3 inches high, described above. The smelting continues during 12 to 16 hours, being discontinued in the daytime on account of the excessive heat. In the 12 to 16 hours 3 to 4 tons of ore are treated, for which 30 to 38 cwts. of wood charcoal are required. The following may be quoted as the results of several nights' work:—[1]

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[1] Balling, *Metallhüttenkunde*, p. 520.

TABULATED RESULTS.

Night.	Furnace No.	Date.	Time			Ore smelted.		Charcoal used.	Tin obtained		Tin per cent of dry ore.
			From p.m.	To a.m.	No. of Hours	Lbs.	Moisture. Per cent	Lbs.	Blocks.	Lbs.	
1st	1	—	4	7.45	15¾	9177	0·6	4342	66	4644	50·7
	2	—	4	8	16	9079	2·4	4322	72	4975	56·1
2nd	1	2nd to 3rd Nov.	5.45	7.45	14	6881	1·1	3492	59	4097	60·1
	2		5.45	8	14¼	6806	1·1	3492	58	4140	61·5
8th	1	—	6	6.45	12¾	7018	2·6	3411	58	4142	60·3
	2	—	6	6.45	12¾	7061	2·5	3492	59	4262	61·9

The smelting of slags and residues containing tin follows immediately after the ore smelting.

The slags obtained in the above smelting of ore are subjected, immediately after the ore smelting, to a repeated smelting in the same furnace; a great part of the tin contained in them is thus extracted.

In the districts of Perak in the Malay Peninsula, 26 cwts. of tin are produced in 12 hours with a consumption of an equal weight of charcoal. The newer furnaces, figured and described above, are employed.

THE EXTRACTION OF TIN FROM THE INTERMEDIATE PRODUCTS AND DROSSES OBTAINED IN THE TREATMENT OF TIN ORE

In the production of crude tin from tin ore the following intermediate products and drosses are obtained, viz.:—slag containing tin, hardhead and the scum formed on the surface of the bath of metal in the tapping pot after the tin has flowed from the furnace; also flue dust and furnace refuse (*e.g.* old bricks, &c., which carry tin).

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[1] Communication by Herr Neeb, from the *Jaarboek v. h. Mijnwezen in Nederlandsch Oost-Indie*, 1878, part ii., pp. 29-99.

Slags from reverberatory furnaces.—These, which are described on page 398, are divided into three parts, one of which is thrown away, another is smelted to extract its tin, and the third is stamped and washed and the richer portions of it thus obtained also smelted to extract the tin which it contains.

The slags which are removed from the surface of the tin in the tapping pot, in which no prill is visible, are thrown away.

Those in which prill is visible are stamped and washed, and the rich headings thereby obtained smelted in reverberatory furnaces, yielding slag-tin, and slag which can be thrown away.

The slags which remain on the bed of the furnace after it has been tapped (spongy slags), and are mixed with large quantities of tin, are usually smelted with charges of ore, but sometimes they are smelted with the rich headings from the stamping and washing of slag.

Slags from shaft furnaces, described on page 407. These, as has already been explained under the extraction of tin, are subjected to repeated smelting, the so-called *verändern* and *treiben* respectively in the shaft furnaces. The slag from the *treiben*, if worth it, is dressed, and the product, a slag rich in tin, is fit to be again smelted by adding it to charges of ore or slag. The tin obtained by smelting slag, the so-called slag-tin, is at least as pure as that obtained from smelting ore.

The first smelting of slag (*verandern*) takes place usually immediately after the ore smelting, and in the same furnace. The smelting of the slag obtained from the first smelting, the so-called *treiben*, is performed in the same furnace immediately on the conclusion of the first smelting, or in special shaft-furnaces, known as *treiböfen*. The slag from the *treiben* is either thrown away, or if sufficiently rich in tin, submitted to a dressing process. These furnaces are *spuröfen*, and are of less height than the ore furnaces, in order to prevent as far as practicable the reduction of iron. Those in Saxony are 5 feet 6 inches high, and have a depth (*i.e.* from back to front) at the top of 2 feet 10 inches, and at the bottom of 2 feet 4 inches. The cross section of the cavity is trapezoidal in shape, the front and back walls being parallel. At the mouth, the front is 1 foot 6 inches wide, and the back 2 feet 3 inches: at the bottom of the cavity the front is 1 foot 3 inches, and the back 1 foot 7 inches in width.

Other residues and drosses from the treatment of tin ore and from the refining are added to the slags when the latter are smelted. A higher pressure of blast is used in smelting slag than in smelting ore.

The so-called hardhead, the tin-iron alloy referred to above, is obtained in slag smelting in addition to slag and tin.

The composition of a slag produced by slag smelting at Schlaggenwald in Bohemia, is given in the following analysis by Lill[1]:—

SiO_2	24·06	per cent.
WO_3	24·03	„ „
SnO_2	10·41	„ „
FeO	20·75	„ „
MnO	5·64	„ „
Al_2O_3	9·00	„ „
CaO	3·50	„ „
MgO	0·37	„ „
	97·76	

Berthier gives the following as the composition of a slag from the second slag smelting at Altenwald in Saxony:—

SiO_2	27·5	per cent.
SnO_2	6·3	„ „
WO_3	3·0	„ „
FeO	48·2	„ „
MnO	1·5	„ „
CaO	3·4	„ „
MgO	1·6	„ „
Al_2O_3	8·5	„ „
	100·0	

In Banca the slag produced by smelting ore is smelted with dross in the above described Van Vlanderen's furnaces immediately after the conclusion of the ore smelting; for example, there would be smelted in two furnaces of that type in 12 hours:—[2]

186	lbs.	dry tin refuse.			
2077	„	damp tin refuse	containing	5·51	per cent. of moisture.
12552	„	stamped slag	„	5·51	„ „
7724	„	coarse „	„	3·44	„ „

These would consume 7060 lbs. of charcoal and would yield 78 blocks of tin weighing 5475 lbs.

The slag obtained from this first slag smelting would be again smelted in the same furnace with refuse, producing tin and a third slag. The charge would be:—

7	lbs.	dry tin dross.			
96	„	damp tin dross	containing	1·79	per cent. of moisture.
1145	„	„ fine slag	„	20·35	„ „
1089	„	„ coarse slag	„	2·6	„ „

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[1] *Jahrb. der K. K. Berg-Academie*, vol. 13, p. 64.

[2] Neeb, *loc. cit.*

This would yield 236 lbs. of tin.

The third slag obtained from the above treatment would yet again be smelted for the extraction of its tin :—

9 lbs. dry tin dross.
65 ,, damp tin dross.
418 ,, ,, fine slag containing 6·25 per cent. of moisture.
680 ,, ,, coarse slag ,, 9·0 ,, ,,

which would yield 486 lbs. of tin.

The fourth slag resulting from this last treatment would be stamped and concentrated by washing, the concentrated slag being smelted in smaller furnaces with tin drosses and richer concentrated slags from earlier smeltings. The fifth slag resulting from the above process would be again smelted after being stamped and concentrated. The sixth and last slag thus obtained would be thrown away even though it were not quite free from tin.

Hardhead, the tin-iron alloy which is formed in the smelting of both ore and slag, has already been mentioned at page 407. This is added in the process of slag-smelting, especially in the *treiben* process; it is usually heated strongly with charcoal and suddenly quenched before smelting.

Skimmings formed during the pouring of tin are added during the smelting of ore or slag.

The dust and *furnace refuse* are also smelted with slag; they are usually put through a process of washing before being smelted.

I. B. THE REFINING OF TIN

The tin obtained by the processes described above, known as crude or raw tin, is usually impure and carries different metals, *e.g.*, iron, copper, lead, antimony and arsenic, which deteriorate it. It therefore requires to be freed from these impurities by a process of purification, the so-called refining. This purification consists of either a liquation of the tin or a liquation followed by *boiling* or *tossing*. In the case of a very pure tin like that from Banca, it is only boiled.

In the liquation the pure tin is melted out, while the impurities which are less fusible than the tin, remain behind in the form of alloys, known as *liquation-dross*. In *boiling* and *tossing* each portion of the melted metal is brought into contact with the air and the more easily oxidisable metals thereby separated as oxides.

The purification of tin by liquation only (*pauschen*) is practised in Saxony and Bohemia, while the purification by liquation and *boiling* is usual in England.

a. The Liquation of Tin (Pauschen)

The liquation ("*pauschen*"), or flowing ("*flössen*"), of tin, is done immediately after it has been tapped from the forehearth into the tapping pot, the so-called *pausch-heerd* being used for the purpose. This is an inclined plate of cast-iron with ridges on it, covered with clay; it is 3 feet 7 inches long and 2 feet 4 inches broad, resting on masonry, with a cast-iron pot placed at its lower end. When in use, this plate is covered with a layer of glowing charcoal and the tin is taken from the tapping-pot with a ladle and poured over it; the less fusible alloys remain behind while the purer metal runs off the inclined plate and collects in the pot at its lower end, this being also filled with burning charcoal. It is again ladled out of the pot and poured over the fuel on the plate, and this is repeated until it no longer leaves a residue behind it in passing over the plate.

After this, the residues on the plate are all collected together and beaten with wooden hammers, by which process some tin is liberated and runs into the pot, while the less fusible alloys known as "*saigerdörner*," remain behind.

The tin which has collected in the pot is allowed to cool there until it shows a bluish brilliant surface, whereupon it is at once cast. It is either poured into moulds or on to a level, smooth, polished, copper plate, from 4 feet 2 inches to 5 feet 2 inches long, 2 feet broad, and ½ inch thick. In the moulds it takes the form of ingots or bars; on the copper plate that of sheets 1/10 inch thick. These are taken when cold to a rolling bench where they are rolled together and then beaten with wooden hammers. The rolled tin is known as *rollenzinn* or *bollenzinn*. The residues from liquation, called *zinnpausche* or *zinnkörner*, are essentially a tin-iron alloy containing varying quantities of tungsten and copper. They are usually worked up by adding them to the charge in slag smelting. The composition of liquation dross from Altenwald is shown in the two following analyses:—

	I. Lampadius. Per cent.	II. Berthier. Per cent.
Sn	68·13	72·52
Fe	25·49	26·44
W	5·14	1·04
Cu	0·74	—
	99·50	100·00

b. The Refining of Tin by the English Method

The English method of refining consists of a liquation of the tin in a reverberatory furnace and a subsequent *boiling* or *tossing*. The furnace used for liquation is either the ore smelting furnace or one of similar construction. In such a furnace the charge would be 6 or 7 tons.

The tin melts slowly and runs through the taphole of the furnace into a cast-iron pot placed below it, *H.*, Fig. 288, while the less easily fusible metals, together with some tin, remain behind on the bed of the furnace. Fresh ingots are piled on the bed as those previously charged are liquated. When no more tin runs from the charge, the temperature is raised until the residue on the bed is melted, after which it is allowed to run into a separate pot; here the less fusible metals settle down to the bottom in the form of tin alloys, while the tin, which still contains small quantities of arsenic, sulphur and iron, remains liquid. This tin is cast in moulds, and as soon as a sufficient quantity has accumulated, is again liquated.

The liquation dross and the residue on the furnace bed are once more liquated, after which the infusible portions are either added to charges of slag or thrown away.

The tin which collects in the refining pot (*kettle*), amounting to 6 or 7 tons at one time, is kept at a high temperature by means of a strong fire underneath, while it is being *boiled*, or more rarely, *tossed*.

The boiling consists in introducing into the bath of heated liquid metal a log of green timber. The wood, at the high temperature, undergoes a dry distillation, and the gases and vapour given off set up a bubbling action in the bath of metal. By this means every portion of the mass is brought into contact with the air, the foreign metals and a portion of the tin being oxidised. The oxides collect together in a foamy mass, the so-called *boil-scum*, on the surface of the metal.

The duration of the *boiling* depends on the state of purity to which it is desired to bring the tin; if a high degree of purity be required, the boiling must be continued for many hours. It is continued till the surface of the molten metal, after removal of the scum, is bright and shining, after which the metal is allowed to stand quiet for some time (1 hour, more or less) in order that the heavy metals in the tin, especially copper and iron, may have an opportunity to settle to the bottom. After this, the scum is skimmed off and the metal ladled into moulds. The upper portions of the metal in the pot are the purest, the lower layers being only of common quality; the portions at the very bottom are usually liquated and boiled over again.

The tin from the upper layers in the refining pot, described as refined tin, goes to the market in the form of ingots or of *grain-tin*.

Tin of second quality, either from the lower layers of the metal in the refining pot—or produced by shorter boiling—goes by the name of common tin.

Grain-tin is made out of the purest block tin: the ingots are heated to a temperature of 200° C., when it becomes brittle and is beaten with a heavy hammer, or it is heated to near its melting point and then allowed to fall from a height of about 3 feet on to a flat stone. Grain tin is principally used in the dyeing and printing of textiles.

Tossing is sometimes resorted to in England instead of boiling. To do this the workman continually takes up a ladleful of the melted metal and pours it back from a height into the pot This method also allows every portion of the mass to be brought into contact with the air. The products from *tossing* are the same as those from *boiling.*

The refining of 6 or 7 tons of tin requires altogether from 5 to 7 hours, viz.,

Liquation	½ to 1 hour.
Boiling according to the purity required .	3 „ 5 hours.
Settling and pouring	1 hour.

Refining by boiling alone, immediately after the metal is tapped from the furnace, is only practicable when the tin is exceptionally pure; it is done in the same manner as the boiling of liquated tin.

c. Purification of Tin by Filtration

Repeated proposals to purify tin by filtration have been made, but so far have not been adopted.

The first proposal of this kind by Lampadius was to filter the tin through quartz sand, or finely divided slag, which was to be previously heated; the result, however, was most unfavourable.

Carter proposed a filter of thin tinned sheet iron, the sheets being about 6 inches long and 4 inches broad. Five hundred of these sheets were to be wedged into a square frame, which was to be fastened in an opening of corresponding size in the bottom of a Passau graphite crucible. When melted tin was poured on to this filter, the tin coating of the tin plate became fluid, and allowed a very pure tin to pass the filter, while a pulpy mass of arsenic, copper, iron and tin remained behind. This proposal has found no practical application; neither has that of Leichsenring, by which the tin was to be allowed to run through sieves of coarse and fine iron wire.

The products of the refining of tin are:—Refined tin, liquation dross and boil scum.

The composition of different qualities of pure tin is shown in the following analyses:—

	From Saxony[1]		From Schlaggenwald.[2]	
	Rolled Tin I. Per cent.	Bar Tin. II. Per cent.	Rolled Tin. III.	Fine Tin. IV.
Sn . . .	99·76	99·93	99·66	99·594
Cu .	—	–	0·16	0·406
Fe . . .	0·04	0·06	0·06	trace
As . .	trace	trace	trace	trace

Banca tin is very pure, and on that account is not refined.

	Banca Tin. I.	 II
Sn . .	99·961	99·99
Fe	0·019	00·2
Pb .	0·014	
Cu . . .	0·006	—

	English Tin I	 II.	 III.
Sn . .	99·76	98·64	99·73
Fe . . .	trace	trace	0·13
Pb	—	0·02	—
Cu .	0·24	1·16	trace

	Tin from Piriac in France. (Loire inférieure) I.	 II.	 III.
Sn . . . ,	99·5	97·0	95·0
Fe	trace	2·8	1.2
Pb	0·2	—	3·0

The impurities in Banca tin from six different districts can be seen from the accompanying analyses[3]:—

	I.	II.	III	IV.	V.	VI
District.	Jebaes	Blinju.	Sungei Liat.	Pankal-pinang.	Merawang	Sungei Slan.
Fe . .	0·0087	0·0175	0·0060	0·0060	0·0070	0·0196
Pb . . .	—	trace	—	—	—	—
S .	0·0099	0·0030	0·0040	0·0027	0·0090	0·0029
C . . .	trace	trace	trace	trace	trace	trace

The Methods of Working up Refinery Dross

The refuse from refining consists of: liquation dross, skimmings and scum from boiling.

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[1] Löwe, *Jahrb. der K. K. Berg-Academie*, vol. 13, pp. 63, 64.

[2] Löwe, *loc. cit.*

[3] *Berg.- und Hütten.-Zeitung*, 1875, p. 454.

The dross from the *pauschen* process is added to the later slag charges.

The residue from liquating tin in a reverberatory furnace is remelted in a similar furnace and run into a small pot, where a difficultly fusible alloy containing tin separates out at the bottom. This alloy is subjected to liquation at a higher temperature in a reverberatory furnace; in this way a portion of the tin is extracted, while hardhead remains in the furnace. This hardhead, if it contain much arsenic, is not worked up any further; if free from arsenic it is added to charges of slag. The composition of the hardhead containing arsenic is:—

Fe	62·50	per cent.
Sn	17·25	„
As	19·02	„
S	1·26	„
	100·03	

The scum from boiling, which consists of oxides of the foreign metals originally present in the ore, with a large proportion of tin oxide and metallic tin, is smelted with carbon in a reverberatory furnace. This yields tin and a black slag which contains prill, mechanically enclosed. The upper layers of tin collected in the tapping pot are sent into the market; while that in the lower portion of the pot is again liquated and boiled. The slag contains, besides prill, only about ½ per cent. of combined tin, and, after being stamped and the tin picked out, is thrown away.

I. C.—THE EXTRACTION OF TIN FROM SKIMMINGS AND OTHER BYE-PRODUCTS.

Among these bye-products may be mentioned the drosses from melting tin, the so-called tin ashes, and the skimmings from the refining of crude lead which contains tin. Of other forms of refuse, tin plate cuttings may be quoted as a type.

Dross produced in the fusion of tin is added to charges of ore when smelted, or in the refining; should they be, however, in considerable quantity, they are sometimes smelted by themselves, in either shaft furnaces or reverberatory furnaces, the slag obtained being stamped and washed to extract the prill.

Before being treated in reverberatory furnaces, the drosses are formed into lumps, which are first liquated. The residue from this operation is sieved to separate the pulverulent portion, and then melted in a small reverberatory furnace on a sand-bed. The tin obtained in this way is known as *aschen-zinn* (ash- or dross-tin). The slags are stamped and washed, the richer portions being smelted after the removal of prill by sieving.

Lead ores containing tin are worked at Freiberg. The tin collects with the silver in the lead, and is separated during cupellation, in the earlier less fusible scoriæ. These are worked up by a process devised by Plattner.[1]

The composition of the scoriæ which contain tin is as follows:—

PbO	70·35 per cent.
SnO_2	12·53 „
Sb_2O_5	12·50 „
As_2O_5	4·73 „
CuO	0·61 „
Ag	0·25 „
	100·97 „

These are first converted into work-lead, and litharge free from silver, by heating them in a reverberatory refining furnace with 5 per cent. of carbon as a reducing agent. The hearth of this furnace is 8 feet 3 inches long, 8 feet broad, and 1 foot 8 inches deep, and is trough-shaped, and in it 4 tons of scoriæ are treated in one day. The consumption of fuel for 100 parts by weight of scoriæ is 12½ parts of coal and 7½ parts of lignite; 100 parts by weight of scoriæ yield 46 parts of work-lead, containing 0·4 per cent. of silver and 53 parts of desilverised scoriæ. The average composition of the latter is:—

Pb	58 per cent.
Sn	11·5 „
Sb	14·5 „
As	7·0 „
Cu	0·2 „
	92·0

These desilverised scoriæ are "fined" (*frischen*) in shaft furnaces with one and a half times their own weight of slag, consuming 25 per cent. of coke, and yielding tin-lead, containing:—

Sn	11·8 per cent.
Sb	10·3 „
As	3·5 „

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[1] *Jahrb. für das Berg.- und Hüttenwesen in Sachsen*, 1888.

This product, known as *zinnfrischblei*, is converted by an oxidising roasting in a refining furnace, into scoria which contains tin, and antimony-lead containing 15 per cent. antimony. The bed of this furnace is 5 feet 9 inches wide, 11 feet 6 inches long, and 14 inches deep, and the charges are each 2 tons in weight.

The scoria separated in this process, known as *erste zinnpuder* ("first tin powder"), does not melt, and has a yellow colour, on account of the lead contained in it. Its composition is the following:—

Pb	68·83 per cent.
Sn	10·85 „
Sb	11·89 „
As	3·0 „
Cu	0·56 „
	95·13

3½ tons of this *zinnfrischblei* are worked up in 24 hours, consuming 20 parts of coal and 15 parts of lignite per 100 of *zinnfrischblei*.

The *erste zinnpuder* is smelted in a shaft furnace with twice its weight of slag from the same process, or with slag from the first "fining" process. The coke used is 60 per cent. of the weight of *zinnpuder*, and the product is called *second zinnfrischblei;* each furnace smelts 7½ tons per day.

This *second zinnfrischblei* is further converted into *antimony-lead* and *second zinnpuder* by an oxidising roasting in a reverberatory furnace. These substances contain:—

Antimony-lead.	Per cent.
Sb	18·0
As	1·0
Sn	0·5

Second Zinnpuder.	Per cent.
Pb	44·74 to 49·86
Sn	27·59 „ 24·28
Sb	13·22 „ 11·97
Cu	0·95 „ 0·48
As	2.72 .. 0·95

The second *zinnpuder* is smelted in a *sumpf-ofen* in charges of 25 lbs. with 5 lbs. of coke, and yields tin-lead. This furnace is one with a deep receptacle at the bottom, in which the metal collects, below the tuyeres; it is 8 feet high and is provided with 2 tuyeres; it is 2 feet wide on the tuyere wall, and 1 foot 4 inches wide on the front wall, and 1 foot 7 inches deep. The nozzles are 0·8 inch diameter, and the blast is worked under a pressure of 0·6 inch of mercury; 1¾ tons of *zinnpuder* are put through in the day. The tin-lead is re-melted in a cast-iron pot, and, after the removal of the dross, contains:—

Sn	33 per cent
Sb	14
As	1

The slag obtained in the smelting of *zinnpulver* contains considerable quantities of tin, both in a state of mechanical inclusion (up to 15 per cent.) and also in chemical combination. The following analysis gives its composition:—

SiO_2	28·65 per cent
SnO_2	20·40
PbO	5·81
CuO	0·15
FeO	26·61
MnO	0·37
ZnO	0·70
Al_2O_3	12·00
CaO	3·15
MgO	0·79
S	0·08
	98·71

This is smelted in a shaft furnace by itself with 20 per cent. of coke, yielding the so-called *slag-tin-lead* and a slag which can be thrown away.

The former (the *slag-tin-lead*) contains:—

Sn	32·6 per cent
Sb	14·6
As	0·7

The composition of the latter is shown in the two following partial analyses:—

	I	II
SiO_2	29·82	30·8
SnO_2	5·3	8·8
PbO	1·54	1·7
CuO	0·18	—

The *slag-tin-lead* is melted in cast-iron pots, as the tin-lead is, and, like the latter, is an article of commerce.

Tin Cuttings

Cuttings from tinned plate, which contain from 3 to 9 per cent. of tin, are worked up most usually by wet methods, to extract the tin they contain. Dry methods have been proposed by (1) Gutensohn, (2) Laroque, and (3) Edmunds.

(1) Gutensohn's method consists in heating the cuttings with sand in *revolving cylinders*; the tin is melted off the iron, and takes the form of small grains; it is afterwards separated from the sand by sieving.

(2) Laroque proposes to heat the cuttings with powdered charcoal and 0·5 per cent. of salt in a pot. This pot is fitted in the middle with a perforated diaphragm. The upper portion of the pot is heated to redness, while the portion below the diaphragm is cooled in water. The tin melts in the upper part of the pot, and falls through the diaphragm into the cooler region, where it collects.

(3) Edmunds uses centrifugal machines, in the centre of which a fireplace is situated. The melted globules of tin are driven through the sieves of the apparatus and collect in the outer space of the machine.

II. The Extraction of Tin in the Wet Way

Wet methods are used to extract tin, and to prepare tin salts from tinned-sheet cuttings and from the waste water from dye works which contains tin. It has also been attempted to apply them to the refining of tin.

Extraction from Tinned-plate Cuttings.—A large number of methods have been proposed for this purpose; of these we shall only mention the most important.

Muir dissolves the tin from the cuttings in hydrochloric acid and precipitates it from the solution by means of zinc; steam is led into the solution during the precipitation. Milk of lime precipitates first the zinc and then the iron from the residual liquor.

Schultze[1] treats the cuttings with acidified ferric chloride solution, and filters the resulting solution, which contains stannous and ferrous chlorides, through a mixture of stannous and ferrous oxides till it is saturated; after this the tin is precipitated by means of metallic iron. This is only possible if the solution be completely neutralised and contain stannous salts.

Moulin and Dolé's method consists in allowing gaseous hydroloric acid to act on the cuttings until the iron is attacked. The sulting salts are dissolved out in water and the tin thrown do[illegible] nc; the precipitate is washed with dilute sulphuric acid, [illegible] sed, and cast in moulds.

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[1] *Berg.- und Hütten.-Zeitung*, 1894, p. 208.

The so-called *argentin*, used in cloth-printing and in the manufacture of silver paper, is prepared by precipitating tin from an idified solution of a tin salt by means of sheet zinc. The tin-sponge hich is obtained is washed and dried, and then ground to fine wder under water and passed through a sieve of hair or silk.[1]

Reineck'en-Pönsgen and Kopp treat the cuttings in revolving rrels with soda lye, litharge and steam; sodium stannate is rmed with the separation of lead according to the following uation:—

$$Sn + 2NaHO + 2PbO = Na_2SnO_3 + 2Pb + H_2O.$$

ie sodium stannate is either evaporated to dryness and sold as *eparing salt*, or the solution of it is precipitated by a stream of rbonic acid and the resulting oxide smelted with charcoal and alk in a reverberatory furnace.[2] The spongy lead which separates it during the process is heated in a current of air, and converted to litharge, which is used over again.

It has also been proposed to treat the cuttings in revolving linders with quicksilver, and to separate the latter from the tin nalgam by distillation.

Hunter of Philadelphia proposed to treat the cuttings with a rm solution of copper sulphate.[3] The tin is dissolved as sulphate d metallic copper is deposited. When the tin is all dissolved and e iron is exposed, the latter precipitates the tin from solution, and dissolved with the formation of ferrous sulphate. The deposit of pper and tin thus obtained is melted up together forming an alloy, it is treated by well-known methods to separate the metals.

Waste Waters of Dye Works.—Tin in these is precipitated by eans of granulated zinc or zinc powder, and the resulting spongy ı dried and fused with borax at a white heat; by this treatment the ıc is volatilised.

Many proposals have also been made for the preparation of salts tin from tinned-plate cuttings.

Tin chloride is prepared at Uetikon, on the Lake of Zurich,[4] by treating the cuttings with dry chlorine gas. The process is conducted in a fixed iron cylinder 13 feet high and 3 feet 3 inches [illegible] diameter, fitted with a perforated false bottom, on which the cuttings are placed, the chlorine being introduced below it. The tin is converted into stannic chloride which collects as a fuming liquid in a receiver under the cylinder. By cautious addition of water *solid tin chloride* is precipitated, which is sold in that form, and is used in dyeing.

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[1] Mullerus, *Chemiker-Zeitung*, 1891, No. 64.

[2] *Der Maschinenbauer*, 1879, p. 80.

[3] German patent, class 40, No. 78,344, January 3, 1894.

[4] Lunge, *Bericht über die Chem. Indust. auf der Schweitzer Landes-Ausstellung in Zurich*, 1883. *Zurich*, 1884, p. 29.

Donath's process is one in which the cuttings are boiled with concentrated soda lye and pyrolusite; the solution of sodium stannate which is obtained is treated with acetic acid to precipitate stannic acid.

Scheurer-Kestner prepares sodium stannate by moistening the cuttings in a current of air with soda lye of 18° to 20° B.

Carez's method is to act on the cuttings with a solution of alkaline polysulphides containing salammoniac. The solution is from 30° to 50° or 60° B. in strength. Any lead which may be present is separated as lead sulphide and the tin is dissolved, being afterwards precipitated by hydrochloric acid as sulphide of tin.

Lambotte proposes to expose the cuttings at a temperature of 100° C. to a stream of chlorine and air, and condense the escaping vapour of stannic chloride, or to lead it into a dilute solution of tin chloride.

Kunzel[1] treats the cuttings with hydrochloric acid or nitric acid, precipitates the tin from the solution by zinc, dissolves the resulting spongy tin in hydrochloric acid, and allows the stannous chloride to crystallise. The residual liquors are worked up for the production of green vitriol or iron.

The Purification of Tin in the Wet Way

This is very costly and is only used in exceptional cases, as for instance when it is desired to prepare tin compounds from pure tin. It consists in dissolving granulated tin in hydrochloric acid; as long as the tin is in excess, the impurities remain for the most part in the undissolved portions. The tin is precipitated from the solution by zinc and the spongy deposit washed with dilute acid and with water.

III. THE EXTRACTION OF TIN BY ELECTROLYTIC METHODS

The proposals which have hitherto been made, for the application of electro-metallurgical methods to ores and slags, do not seem to have much chance of success; but those for the treatment of tinned plate cuttings, and for refining tin, by these methods, appear to be more likely to succeed.

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[1] *Berg.-und Hütten Zeitung*, 1874, p. 57.

Treatment of Ores—For this, Burghardt,[1] and Vortmann and Spitzer,[2] have proposed methods. Burghardt proposes to fuse the finely divided ore with excess of caustic soda, to extract the sodic stannate from the fused mass with water, and to separate the tin from the solution by an electric current. Sheet iron is used for the anodes, and plates of tin, iron, or some other metal for the cathodes. The temperature of the solution for electrolysis should be 60° C. If arsenic, antimony or sulphur be present in the ores, they should be removed by roasting before the ore is fused with caustic soda. According to Borchers[3] the current is soon interrupted by the deposition of oxides of tin on the anode plates; he states that it is impossible to extract tin with profit in this way.

Vortmann and Spitzer's method consists in converting the tin of the ores or drosses, previously freed from sulphides, into sodium sulphostannate, by fusing them with three times their weight of a mixture of 2 parts of soda-ash to 1 of sulphur. The solution of sulphostannate, after the addition of ammonium compounds, is electrolysed between anodes of lead and cathodes of tinned sheet-copper. Borchers[4] points out that there is no material which can stand the production of sulphostannate by a process of smelting; even in a reverberatory furnace its production is said to be possible only with great loss of tin and high cost for repairs. This method has not found any practical application.

Shears[5] has proposed the following method for the recovery of tin from slags. The slags are first fused with alkalis and the alkaline stannate lixiviated out with water. The tin is precipitated from the solution by the electric current in the way described above. Silica and alumina are precipitated from the residual liquor by milk of lime and are used for the manufacture of cement; the alkali is recovered by usual methods for use again.

If wolfram is present, it is found in the last liquors, and can by evaporation be separated as tungsten salts. This method has also found no application.

A long series of methods has been suggested for the recovery of tin from tinned plate cuttings by means of the electric current, as, for instance, the methods of Keith, Gutensohn, Walbridge, Beatson,

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[1] German patent, No. 49,682, 1 July, 1889.

[2] *Ibid.*, No. 73,826, 14 Sept., 1893.

[3] *Electrometallurgy*, p. 154.

[4] *Loc. cit.*, p. 301.

[5] English patent, No. 9,821, 14 June, 1889.

Price-Fenwick, Morin, Minet, Smith, and Vortmann and Spitzer. These for the most part, however, do not appear to have come into use. Both basic and acid electrolytes have been suggested.

Borchers[1] has proposed to use for this purpose as an electrolyte, a 12 to 15 per cent. solution of common salt, containing 3 to 5 per cent. of sodium stannate. In consequence of the high conducting power of salt solution, this electrolyte serves much better than pure sodium stannate for the purpose. With a current of 50 to 150 ampères per square metre and a potential of 2 to 3 volts, he obtained from cuttings (free from solder) a spongy metallic precipitate, the temperature of the bath being from 40° to 50° C.; the precipitate, after washing and drying, could be melted and cast. The bath must be kept distinctly alkaline; as the quantity of tin oxide in the bath increases, alkali must be added. Towards the end of the process the solution becomes so concentrated that it is more profitable to work it up for *preparing salt*, by evaporating it to dryness, than to continue the electrolysis. The advantages of this process are stated by Borchers[2] to be, the possibility of completely removing the tin from the cuttings, the production of a residue of clean sheet iron, the possibility of producing a tin quite free from iron, the practicability of using an iron vessel which itself forms the cathode, and the use of an iron basket as anode.

Keith uses as electrolyte a solution of caustic soda and sea-salt. The mixture is placed in an iron pan, and the cuttings, which are connected with the positive pole, are hung in the electrolyte in a basket. The wall of the vessel serves for a cathode.

Beatson[3] uses a hot solution of soda, to which potassium cyanide has been added. Iron plates are used as the anode, or the wall of the vessel, if it is made of iron, serves the purpose. It must be pointed out that a solution of potassium cyanide is rapidly decomposed when kept at the boiling point.

According to a new patent[4] the inventor uses a solution of alkaline hydrate as electrolyte, and the deposit of tin obtained is electrolytically purified in a solution of tin chloride; in order to obtain the tin in a compact form it is deposited on revolving rolls.

Price[5] uses soda lye as electrolyte; there are others who do the same.

Walbridge makes use of a solution of caustic soda and sodic nitrate for the purpose.

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[1] *Lor. cit.*, p. 154. [2] *Loc. cit.*, p. 396.

[3] English patent, No. 11,067, 18 Sept., 1885.

[4] *Ibid*, No. 12,200, 1892. [5] *Ibid*, No. 2,119, 1884.

Gutensohn,[1] Fenwick,[2] and Naef, use chloride of tin as the electrolyte.

Changy makes use of a solution of stannous chloride to which ammonium chloride or hydrochloric acid has been added.

Raymond's proposal is to adopt a solution of stannous chloride at 5° to 6° B. acidified with hydrochloric acid, and to lead the current into the bath through iron rods.[3]

The following method, invented by Smith, is said by F. Fischer[4] to have been tried in Berlin and in England. Diluté sulphuric acid is the electrolyte, and tinned copper plates are used as the cathode. The tin cuttings themselves form the anode: they contain from 3 to 9 per cent. of tin and are suspended in a wooden cage in the liquid. The vats are lined on the inside with caoutchouc. The cuttings are bound together with long strips of tinned iron, and by the copper wire which carries the current. The dynamo gives a 240 ampère current with an electromotive force of 15 volts, and absorbs 7 horse-power. The baths are 8 in number and are 5 feet by 2 feet 4 inches by 3 feet 3 inches in size. Each set of four is formed by placing divisions in a wooden vat 10 feet by 5 feet. The cathodes, 4 feet by 3 feet by 0·06 inch, are suspended vertically in front of the anodes at distances of 4 inches apart.

The electrolyte is made by diluting 1 part by measure of sulphuric acid at 60° B. with 9 parts of water.

The tin separates in the form of a sponge as long as the solution is acid, but as the bath becomes more and more neutral the deposit becomes pulverulent and even crystalline; it is purer than ordinary commercial tin and dissolves more rapidly than the granulated metal in acids; it is therefore used for the preparation of tin salts. As soon as the tin is removed from the surface of the iron, the latter is attacked and collects in such quantities in the electrolyte that the latter must be renewed every seven weeks; it is worked up for the manufacture of green vitriol.

According to theory, 240 ampères in 8 baths should yield per hour 9·37 lbs. of tin; actual working, however, produces only the half of this amount. The principal reason for this proportionally small performance is that the current dissolves iron as well as tin as soon as the former is exposed.

Vortmann and Spitzer proposed that their above-mentioned method for the extraction of tin from ores should also be applied to the recovery of tin from cuttings. The conversion of tin into sodium sulphostannate was to be effected by heating the cuttings with half their weight of a mixture of sulphur and soda-ash.

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[1] German patent, No. 12,883.

[2] English patent, No. 8,988, of 1886.

[3] *Electrotech. Zeitschr.*, 1892, p. 573.

[4] Wagner-Fischer's *Jahresberichte*, 1885, p. 173.

Sulphide of Tin, which is a bye-product in the preparation of some organic colouring matters, can be converted into sodic sulphostannate by boiling it with a solution of sodic polysulphides.

The author is not in a position to say if any of the above-mentioned methods have been actually put into operation on a working scale.

The Refining of Tin by Electro-metallurgical Methods.—According to the experiments of A. Brand[1] the refining of tin by the electric current would seem to have some prospect of success. These experiments showed that the tension in a bath with tin anodes and a solution of stannous chloride containing 5040 grains per gallon and 2·5 per cent. by volume of concentrated hydrochloric acid, amounted to 0·058 volt (14·8 ampères); with 7·5 per cent. of hydrochloric acid it was only 0·031 volt.

A current of 1 ampère deposits 2·195 grammes of tin per hour: 455·6 ampères are therefore necessary for the deposition of 1 kilo per hour. The energy required for the extraction of 1 kilo of tin per hour may be calculated as:—

$$0{\cdot}058 \times 455{\cdot}6 = 26{\cdot}424 \text{ Watts};$$

or

$$\frac{26{\cdot}424}{75 \times 9{\cdot}81} = \frac{26{\cdot}424}{735} \text{ H.-P.}$$

The loss of energy, in the conversion of mechanical into electrical energy, may be taken as 12 per cent. Further, the loss due to conversion of electric energy into heat, short-circuiting, &c., may be taken as 25 per cent., so that the actual consumption of energy may be reckoned at

$$\frac{0{\cdot}058 \times 455{\cdot}6}{735 \times 0{\cdot}88 \times 0{\cdot}75} = 0{\cdot}054 \text{ H.-P.}$$

Assuming that one horse-power per hour requires 2 kilos of coal, the coal required for the extraction of 1 kilo of tin would be 0·11 kilo. As the principal impurity of tin, viz., iron, collects in the electrolyte and is not separated from it, fresh quantities of electrical energy will be continually introduced into the circuit.

It must be borne in mind that the loss due to the conversion of mechanical into electrical energy, in the newest machines with high-pressure expansion and condensation, is only 9 per cent., and that in the newest dynamos only 6 per cent. of the original energy goes to waste, a loss of power of only 15 per cent. is therefore a possibility. The loss of current in the performance may be assumed to be 10 per cent. and the coal consumption in the newest steam engines to be 1 to 1·5 kilos per hour per horse-power. In view of these circumstances, therefore, the consumption of coal and power will be less than that indicated above.

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[1] Dammer, *Chem. Tech.*, vol. ii., pp. 27, 28, 324.

ANTIMONY

PHYSICAL PROPERTIES

ANTIMONY is characterised by its great brilliancy and by its colour, silver white with a slight tinge of blue; the latter is increased by the presence of impurities in the metal. When deposited from a solution by zinc it takes the form of a black powder. When melted antimony is allowed to cool slowly, it exhibits a coarsely foliated structure; rapid cooling makes it granular and crystalline. Antimony crystallises, like the isomorphous metals bismuth, arsenic and tellurium, in the forms of the hexagonal system. Its specific gravity has been determined to lie between 6·6 and 6·8. Schröder has given it as 6·697 compared with water at 4°C.

Antimony is brittle and can be easily powdered in a mortar. It is harder than copper. Its coefficient of linear expansion by heat between 0° and 100°C. is, according to Calvert and Johnson, 0·000985. It melts between 440° and 450°C. (Pictet). In passing from the liquid to the solid state it does not expand like bismuth does. Carnelly and Carleton-Williams state that its boiling point is between 1090° and 1450°C. According to Demarcay it boils in a vacuum at the temperature of 292°C. It burns in the air forming oxides, but can be distilled in a stream of hydrogen.

When pure molten antimony is allowed to solidify slowly and without disturbance under a layer of slag, a fern-like appearance, of raised lines radiating from the centre, appear on the solidified surface of the metal. This is the so-called "antimony star" or "regulus antimonii stellatus." On small castings there will be only one such star in the middle of the surface, but larger castings will show many intersecting ones.

This appearance is not produced in impure antimony nor in the pure metal unless it is kept very still and covered during cooling by a layer of slag. As it is generally regarded as an indication of the purity of the metal, pure antimony, which does not possess *it*, is always re-melted and cooled under the required conditions.

Its specific heat, as determined by Regnault between 0° and 100°C., is 0·0508. Its conductivity for heat, compared with that of silver as 1000, was determined by Calvert and Johnson: along its axis of crystallisation it is 215 and at right angles to this direction it is 192. Its electrical conductivity, compared with that of silver as 100, is 4·29 at 18·7°C., according to Matthiessen.

Commercial antimony is generally contaminated by small quantities of sulphur, arsenic, lead, copper and iron. These cause the abovementioned blue tinge in its colour.

PROPERTIES OF ANTIMONY AND OF ITS COMPOUNDS WHICH ARE OF IMPORTANCE FOR ITS EXTRACTION

Antimony is not affected by exposure to air at ordinary temperatures, but at temperatures above it melting point it oxidises rapidly. Metal which has been reduced from the oxides by charcoal in presence of alkalies frequently tarnishes in the air. The cause of this is said to be a small quantity of alkali which is retained by the metal and absorbs moisture with liberation of hydrogen.

When antimony, which has been raised to a red heat, is allowed to fall from a sufficient height on to a plate, it is dissipated in a mass of brilliant sparks, forming a dense white cloud of oxide.

Antimony is attacked by hydrochloric acid only when it is in the state of very fine powder: hydrogen is then liberated. Sulphuric acid does not attack it, when dilute: the hot concentrated acid however forms with it antimonious sulphate, sulphur dioxide being at the same time liberated. Nitric acid attacks antimony, producing, according to its temperature and degree of concentration, a mixture of the trioxide and tetroxide of the metal in different proportions. These oxides are insoluble in the acid.

Aqua regia in the cold dissolves antimony easily, forming the penta-chloride.

In a current of steam at a red-heat, antimony is slowly converted into oxide.

When ignited with nitre and soda it explodes, forming an alkaline antimoniate: with a smaller proportion of nitre it also forms some trioxide.

The metalloids, with the exception of boron, carbon and silicon, all form compounds with antimony.

Antimony Hydride, SbH_3

Antimony forms only one compound with hydrogen, antimonuretted hydrogen. This is a colourless imflammable gas, which burns with a greenish flame producing a white smoke of steam and antimony trioxide. It is formed when hydrogen is generated in the presence of a soluble antimony compound, or when alloys of antimony with the alkali metals are decomposed by water, or when an antimony-zinc alloy is treated with sulphuric or hydrochloric acid. When this gas is led through a heated glass tube, antimony is deposited in the cold part of the tube in the form of a mirror. If a mixture of this gas with hydrogen be passed through a solution of silver nitrate, a black precipitate of silver antimonide, $SbAg_3$, and silver is deposited.

OXIDES OF ANTIMONY

Antimony forms three oxides: (1) Antimony trioxide, Sb_2O_3, (2) Antimony tetroxide, Sb_2O_4, and, (3) Antimony pentoxide, Sb_2O_5. The pentoxide forms two acid hydrates—Antimonic acid, $HSbO_3 + 2H_2O$ and metantimonic acid, $H_4Sb_2O_7$.

Antimony Trioxide, or Antimonious Oxide, Sb_2O_3,

is formed by heating antimony or sulphide of antimony in the air; it is a white powder which becomes yellow when heated, regaining its whiteness on cooling. It melts at a dark red heat forming a yellow liquid which solidifies to a grey mass resembling asbestos. It is volatile, and can be sublimed. If heated in the air it is converted into the tetroxide which is not volatile. If the vaporised trioxide and air be passed over ignited, finely divided oxides of those metals which form compounds with antimonic acid, the latter is formed and combines with the oxides producing antimoniates.

It is insoluble in water, sulphuric acid or nitric acid, but is easily dissolved by hydrochloric and tartaric acid and by caustic alkalies. With antimony sulphide it melts without decomposition, forming the so-called antimony-glass. The trioxide is poisonous, especially in the form of vapour.

Antimony Tetroxide or Antimonic Antimoniate, Sb_2O_4,

is a white powder which is neither fusible nor volatile. It can be prepared by heating the trioxide in the air or by igniting the pentoxide. Hydrochloric acid dissolves it readily. It is a metallurgical product, being known under the name of "antimony ash" or "cinis antimonii," but in this form always contains some trioxide. If the antimony ash be ignited with charcoal and alkaline carbonates, metallic antimony is obtained; if the alkali be omitted, the greater portion of the antimony will be volatilised as trioxide, a small part only being obtained in the metallic state.

If the tetroxide be fused with metallic antimony in the proper proportion, the trioxide is formed:—

$$3Sb_2O_4 + 2Sb = 4Sb_2O_3.$$

When the tetroxide is fused with antimony sulphide in suitable proportions, sulphur dioxide is liberated, and the trioxide is formed, which, however, always retains more or less of the sulphide:—

$$Sb_2S_3 + 9Sb_2O_4 = 10Sb_2O_3 + 3SO_2.$$

This impure trioxide of antimony, the colour of which varies with the quantity of sulphide it contains, is known as "antimony-glass," and is used as a colouring matter in glass making, more especially in the preparation of artificial gems.

Antimony Pentoxide or Antimonic Anhydride, Sb_2O_5

This is a bright yellow powder and can be prepared by treating antimony with nitric acid. The powder obtained must be repeatedly evaporated to dryness with nitric acid to completely oxidise the tri- and tetroxides which are at first formed, and the residue gently ignited.

The pentoxide is insoluble in water and in nitric acid, but dissolves slowly in concentrated hydrochloric acid; it is converted on ignition into the tetroxide.

Antimonic anhydride forms two hydrates, each of which forms a series of salts, viz.:—

Antimonic acid, $HSbO_3 + 2H_2O$, and
Metantimonic acid, $H_4Sb_2O_7$.

Antimonic acid is used to replace arsenic acid in the manufacture of aniline yellow and aniline red.

CHLORIDES OF ANTIMONY

Antimony forms two compounds with chlorine, viz.:—

Antimonious chloride or antimony trichloride, $SbCl_3$, and
Antimonic chloride or antimony pentachloride, $SbCl_5$.

The trichloride is formed when antimony trisulphide is boiled with concentrated hydrochloric acid; also when the metal or the trisulphide is heated with corrosive sublimate. It is soluble in hydrochloric acid, is volatile, and can easily be distilled. When the solution of it in hydrochloric acid is diluted with water, white basic chloride of antimony is precipitated: this is known as "powder of Algaroth," and was formerly used in medicine.

The pentachloride is formed with evolution of light when chlorine acts on antimony. According to Gore, antimony in the form of a grey amorphous mass is deposited when a strongly acid solution of the pentachloride is electrolysed. This contains, in addition to small quantities of free hydrochloric acid, from 3 to 20 per cent. of antimony pentachloride, and explodes if heated to 200°C.

SULPHIDES OF ANTIMONY

There are two compounds of sulphur and antimony, viz.:—

Antimony trisulphide, Sb_2S_3, and
Antimony pentasulphide, Sb_2S_5.

The trisulphide is known in both the crystalline and the amorphous condition. The crystalline form is found in nature as antimony glance or stibnite; it possesses a greyish black colour, metallic lustre and crystalline structure. It can be melted out of contact with the air at a red heat, and volatilises without decomposition at a strong white heat.

The amorphous trisulphide can be prepared artificially, and possesses, according to the method of its preparation, a red or orange colour.

The red trisulphide, which formerly was used in medicine under the name of "Kermes mineral," can be prepared by boiling antimony glance with carbonate of potash or soda. The antimony sulphide is deposited from the solution on cooling as a reddish-brown powder. It always contains variable quantities of antimony trioxide and alkali.

The orange-coloured trisulphide can be obtained by precipitating a solution of an antimonious salt with sulphuretted hydrogen: this precipitate always contains water. The so-called *antimony cinnabar* is a red amorphous trisulphide containing the trioxide; it is prepared by treating a solution of antimony in hydrochloric acid with thiosulphate of calcium or thiosulphate of sodium. It is used as a pigment in oil painting, on account of its fiery red colour.

When antimony sulphide is calcined in a current of air, antimony trioxide and sulphur dioxide are formed, the former being partly volatilised, and partly converted into the tetroxide; the sulphate is not formed. The trisulphide is easily fused, and therefore the roasting of it is difficult.

A mixture of air and steam when passed over the trisulphide forms the trioxide with liberation of sulphuretted hydrogen; in this case also the sulphate does not appear to be produced. Antimony is reduced from the trisulphide at a red heat by the action of hydrogen, hydrocarbons, iron and zinc. According to Karsten, charcoal has the same effect, but only at a temperature above the boiling point of the metal.

The trisulphide is soluble in hot concentrated hydrochloric acid, forming antimony trichloride. If it be treated with a solution of a caustic alkali or an alkaline carbonate, or of an alkaline sulphide, or if it be fused with these bodies in the solid state, substances called *sulphantimonites* are produced, *e.g.*

$$2Sb_2S_3 + 4KOH = 3KSbS_2 + KSbO_2 + 2H_2O.$$

These *sulphantimonites* are soluble in water when they contain a large proportion of basic sulphides, but a large proportion of antimony renders them insoluble. The trisulphide and the trioxide do not mutually decompose each other as is the case with galena and litharge, but fuse together undecomposed to form the so-called *antimony-glass.*

When the trisulphide is fused with the penta- or tetroxide, sulphur dioxide and the trioxide are formed: the latter takes up some of the undecomposed trisulphide and forms with it *antimony-glass.*

The pentasulphide of antimony, Sb_2S_5, is an orange-coloured powder, known in medicine as *golden sulphide of antimony.* It can be obtained by the action of sulphuric acid on the so-called sulphantimoniates. These latter substances are prepared by boiling antimony glance with a solution of an alkaline polysulphide, or by fusing the two substances together in the solid state. *Schlippe's salt,* $Na_3SbS_4 + 9H_2O$, is one of these sulphantimoniates.

The pentasulphide, when treated in the absence of air, yields the trisulphide, sulphur being separated.

Hydrochloric acid converts it into the trichloride with separation of sulphur. In other respects the pentasulphide behaves like the trisulphide. It is used principally, at the present time, as a red pigment and for vulcanising india-rubber.

OXY-SALTS OF ANTIMONY

The most important of these is *tartar emetic* or potassium stibnyl tartrate, $C_4H_4K(SbO)O_6$, used in medicine.

ALLOYS OF ANTIMONY

Antimony alloys with most metals, making them brittle. It is added to lead to harden it. When alloyed with tin it renders it silvery in appearance, increases its hardness, and raises its melting point.

The most important alloys of antimony are *type-metal*, which consists of lead, tin and antimony, or of only lead and antimony; *hard-lead*, produced by working lead ores which contain antimony, and which consists of lead and antimony in very varying proportions; *britannia-metal* and *white-*, *bearing-*, or *antifriction-metal*, which consist principally of antimony and tin, with addition of lead, copper, zinc, bismuth and nickel. *Britannia-metal*, which is used for the manufacture of teapots, spoons, plates, &c., contains, according to Ledebur, tin 85 to 93 per cent., antimony up to 10 per cent., and copper up to 3 per cent. English *plate pewter* and *queen's-metal* are similar alloys.

ANTIMONY ORES

Antimony Glance, S[illegible]

Antimony glance is the most importa[illegible]f antimony: it is also known by the following names—*grey antimony ore*—*antimonite*—*stibnite*. It contains 71·77 per cent. of antimony and 28·23 per cent. of sulphur. It occurs in long rod-like or needle-like rhombic crystals, or in the massive state, or disseminated in fibrous or compact particles. It frequently contains gold and silver, and usually arsenic also; its more commonly associated minerals are quartz, calc-spar, heavy-spar and spathic iron ore; zinc blende and galena frequently occur intimately mixed with it.

It occurs in Germany (Arnsberg, Erzgebirge, Fichtelgebirge, the Harz), in Bohemia (Milleschau, Hatc, Brodkowic, Przibram, Schönberg, Michaelsberg), in Hungary (Kremnitz, Toplitzka, Schemnitz, Felsöbanya, Nagybanya, Dobschau, Rosenau, Gisno, Gross-Göllnitz, Magurka), in Servia, in Bosnia (Serajewo), in France (Auvergne, Gard, Ardèche, Aude, Vendée, Lyonnais, Haute Loire, Bouc, and Septèmes near Marseilles), in Italy (Tuscany), in England (Cornwall), in Spain (Estremadura and Badajoz), in Portugal (Oporto and Braganza), in Algiers (Province of Constantine), in Canada, in the United States (Arkansas, Nevada, Utah, California and Montana), in Nicaragua and in Mexico; in Asia it occurs in Borneo, India, Japan and Asia Minor; in Australia it is found in New South Wales, Victoria and New Zealand. The greatest portion of the ores which are treated in England come from Borneo, Australia and Japan.

Native Antimony

Native antimony occurs but rarely, and is not a source of any importance.

Oxide of Antimony, Sb_2O_3,

otherwise known as *white antimony* or *antimony bloom*, is dimorphous; the rhombic form is named *valentinite* and the cubic form *senarmonite*; it contains 83·4 per cent. of antimony; it is formed by the weathering of *antimony-glance* or of *native antimony*, and occurs in the upper portions of antimony ore deposits. The localities where this ore occurs most freely are: Sensa and Haminate in the Province of Constantine in Algiers, Borneo, and Sonora in Mexico.

The other antimony minerals occur in comparatively small quantity and do not constitute the basis for special processes. Among these are:—*red antimony ore*, also known as *antimony blende* or *pyrostilbite* ($2Sb_2S_3+Sb_2O_3$), containing 75 per cent. of antimony and found in Tuscany, Canada (Southam), Braunsdorf (Saxony) and Przibram; *antimony ochre* or *cervantite* (Sb_2O_4), occurring in Tuscany. Antimony is also a constituent of many lead-, copper- and silver-ores, especially the latter. Among these may be mentioned *bournonite*, *zinkenite*, *jamesonite*, *plagionite*, *feather-ore*, *wolfsbergite*, *polybasite*, *proustite*, *antimonial nickel*, *antimonial silver*, *miargyrite*, *berthierite*, *boulangerite* and the *fahl-ores*. *Galena* also very frequently contains antimony.

In addition to the minerals mentioned above, the following are sometimes sources of antimony:—(1) Speiss containing antimony obtained in working copper- and silver-ores which contain antimony, (2) Residues, &c., which contain antimony obtained in liquating antimony glance, (3) Dross obtained in antimony smelting. In the working of galena which contains antimony, the latter metal for the most part alloys with the lead produced forming the so-called *hard-lead*.

THE EXTRACTION OF ANTIMONY

The principal source of antimony is antimony-glance; the other ores occur in too small quantity to form the subject of independent processes and are therefore worked with antimony-glance.

The extraction is conducted principally by dry methods; proposals have been made for the use of wet processes and also of electro-metallurgical methods, but these have, as yet, not found practical application.

Antimony obtained by dry methods is always contaminated by foreign metals, and accordingly has to be refined: this is usually done in the dry way.

Sulphide of antimony is used to a large extent, especially as a paint for ships' bottoms: it is therefore the object of preparation in a special industry, which consists in simply liquating it from the other minerals and rocks which accompany it in its ores. The product of this process is called *crude antimony*; metallic antimony is known as *antimony regulus.* The liquation of antimony-glance is also sometimes the first step in the extraction of the metal, but at present is seldom resorted to, although the residues from it are worked up to extract the metal they retain. We have therefore to describe:—

I. The extraction of antimony in the dry way.
II. The proposals for extracting antimony by wet methods.
III. The proposals for extracting antimony by electro-metallurgical processes.

I. THE EXTRACTION OF ANTIMONY IN THE DRY WAY

The treatment of ores containing antimony glance may have for its object, as already explained, either the preparation of crude antimony, or the extraction of antimony regulus. In the latter case the product will need to be refined. We must therefore distinguish between:—

A. The treatment of antimony-glance for the preparation of crude antimony.

B. The treatment of antimony-glance and other ores of antimony for the extraction of the metal.

C. The refining of antimony.

A. THE TREATMENT OF ANTIMONY-GLANCE FOR THE PRODUCTION OF CRUDE ANTIMONY

Ores containing more than 90 per cent. of antimony sulphide are used as crude antimony after being ground, without further treatment. Ores containing less than 90 per cent., and as low as 40 or 50 per cent., are subjected to liquation, if the pieces are of the right size, *i.e.*, larger than hazelnuts, best about walnut size. Small-grained ore and ores with a low percentage of antimony sulphide, are, as pointed out above, worked up for the production of the metal. (Small-grained ore could be worked for crude antimony by fusion in furnaces.)

The liquation of antimony sulphide from its accompanying minerals and rock is possible on account of its comparatively low melting point, below a red heat. The maintenance of the proper temperature is of the greatest importance, for at temperatures above a red heat the sulphide is volatilised and at too low temperatures the residues contain large quantities of antimony. The size of the pieces of ore too has considerable effect on the result; the smaller they are the less complete is the liquation, and the richer are the residues, and further, fine ores lie so close together that the fused sulphide is unable to escape. The best size is proved to be that of walnuts. Fine ores with low percentage of metal give a better result if treated for the production of regulus.

In commerce great importance is attached to the radiated structure of the product: this is obtained by slow cooling of the liquated sulphide; if it is rapidly cooled this structure is absent.

The liquation can be done in closed or in open (reverberatory) furnaces. In closed furnaces the ore is contained in pots or tubes, while in the reverberatory furnace it lies exposed on the bed. The closed furnaces use more fuel, and cost more for labour, than the open ones, but they extract a larger proportion of the sulphide than the latter, which lose considerable quantities by volatilisation and oxidation.

1. LIQUATION IN CLOSED FURNACES

The melting is done in pots or in tubes. If pots are used, they are either directly surrounded by the burning fuel, or are heated by the flame from a fireplace. The latter method is always adopted where tubes are used. Pots are worked intermittently, but pipes permit the adoption of continuous work with corresponding economy in fuel.

a. Liquation in Pots

Pots directly in contact with the fuel are used at Wolfsberg in the Harz, at Magurka, Rosenau, and Gross-Göllnitz in Hungary, at Milleschau in Bohemia and at Malbosc in France. This method requires a high consumption of fuel, but has the advantage that it can be conducted at the mine on account of the simplicity of the furnace. It is therefore used where the ores are rich and fuel (wood or coal) is cheap at the mine.

The pots are made of fireclay and hold from 11 to 56 lbs. In the bottom of each there are 4 or 5 holes 0·4 to 0·6 inch in diameter through which the melted sulphide escapes. These rest on receivers of burnt clay which collect the liquid crude antimony. The receivers, in order to ensure the slow cooling of the contents, are bedded in sand, ashes, or breeze. The pots are placed in a row, there being sometimes several of these at regular distances apart; 20 or 30 pots form one row. The space in which they are placed is enclosed by a low wall of dry masonry. The space between the crucibles and between them and the wall is filled with fuel, coal or wood being used. The liquation takes from 2 to 12 hours according to the size of the charge.

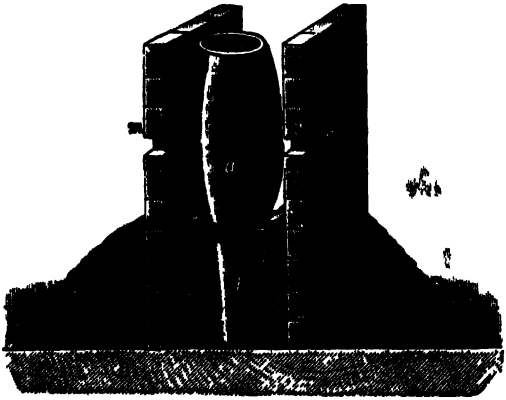

FIG 298.

At its conclusion the pots are lifted off the receivers, emptied and again charged and placed in position. The receivers are in some places emptied after each charge and in others left till they are full. The residues contain as a rule not less than 12 per cent. of sulphide.

Fig. 298 shows the arrangement of an earlier liquation plant at Wolfsberg in the Harz.[1]

Here *a* is the pot with holes in the bottom for the escape of the liquid sulphide, *b* is the receiver surrounded with a bed of non-conducting material to prevent the rapid cooling of its contents, *m* is the wall, which in this instance encloses only one row of pots; it is built of dry masonry and is provided with draftholes. The height of the pot is about 12 inches, the diameter 8 inches, and it holds 22 lbs.

[1] Kerl, *Metallhüttenkunde*, p. 520.

At Malbosc (Ardèche) in France, the charge per pot is 33 lbs. After 4 charges (40 hours) the receiver, being full, is emptied. In the 40 hours 20 pots produce 1,050 lbs. of the sulphide with a consumption of fuel of 3,330 lbs. of coal and 448 lbs. of brushwood.

Pots heated by a flame permit of greater economy of fuel and also facilitate the working of poorer ores, but the labour is more severe on the workmen than in the method previously described. These pots are placed in a furnace on each side of the fire, or are arranged in a circle round it: the receivers for the melted sulphide are either placed below the bed of the furnace surrounded by sand and out of contact with the flame, or they are placed entirely outside the furnace, being connected with the liquation pots by a clay pipe This latter arrangement is much more satisfactory than the former, because it does not necessitate the interruption of the process for the clearing out of the receivers as is the case with the former. Furnaces with the receivers under the bed are employed at La Lincoule in France (Haute Loire), those with exterior receivers are used in Hungary. Fig. 299 shows the construction of one of the latter sort of furnaces:—

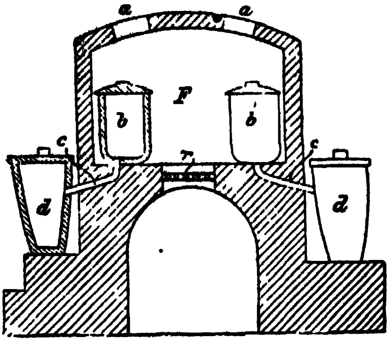

FIG. 299.

F is the heating chamber, *r* the grate, *b*, *b* are the pots fitted with covers, *d*, *d* the receivers, *c*, *c* the pipes connecting the pots with the receivers, *a*, *a* are openings in the roof through which the charges are introduced into the pots. The fuel consumption is higher and the production less in the pot furnaces, and they are inferior to the tube furnaces which are next to be described.

b. *Liquation in Tube Furnaces*

These furnaces can be arranged with vertical or horizontal tubes, but the latter arrangement does not appear to have been adopted. The vertical arrangement is used at Malbosc in France and at Banya in Hungary, and with it more favourable results have been obtained in regard to fuel consumption, quantity treated, and cost of labour, than with the pot furnaces.

The construction of the furnace used at Malbosc is shown in Figs. 300 and 301.[1]

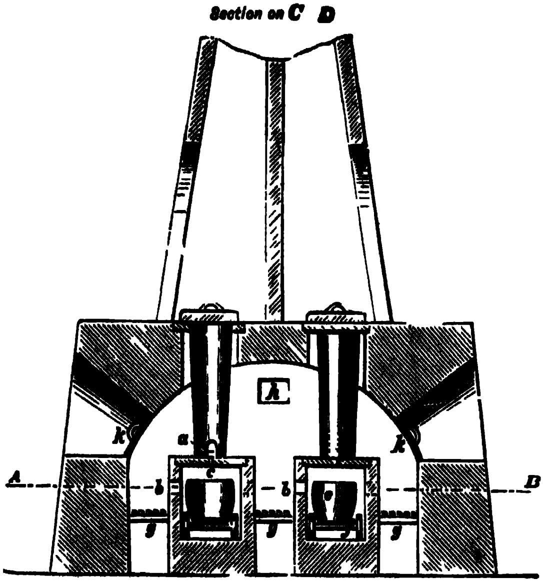
Section on C D

Fig. 300

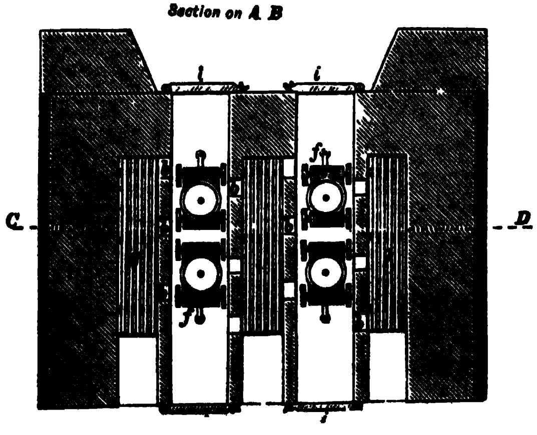
Section on A B

Fig. 301

The tubes are arranged in groups of four, each group being placed in a chamber with 3 grates: they extend to the outside of the roof where they are closed, while working, with a cover, and are 3 feet 3 inches high, 10 inches diameter at the upper end and 7¾ inches diameter at the bottom, their walls being 0·6 to 0·8 inch thick. They rest on a fire-clay slab pierced with holes for the escape of the liquid sulphide; *a* in the figure is a hole in the side of the tube at its lower end through which the residue is cleared out: these holes are 2·7 inches in width and 4·7 inches high, and during the working of a charge are closed with a clay plug or with a luted plate. *e* is the receiver 1 foot 4 inches high and 10 inches wide. These, carried on small waggons, are introduced through the openings with tight fitting doors *i*, *i*, into the chambers shown in the figure: when full they can be replaced by empty receivers without interrupting the operation. The doors *i*, *i* are provided with peepholes through which the progress of the liquation can be observed. The flames play round the tubes and escape through three openings *h*, into the chimney; the flues are provided with dampers by which the intensity of the fire can be regulated. Part of the fire passes through the holes *b*, *b*, 4 inches square, in the walls of the receiver chambers and maintain them and the collected sulphide at the proper temperature. The openings *k*, *k* serve for the removal of the residues from liquation, and for repairing any damage to the tubes. During the working these are closed by cast-iron plates. A newly built furnace requires to be heated to a bright red heat for 48 hours before a charge is inserted. The regulation of the temperature is adjusted according to the colour of the product, which ought to be bluish; a red colour is an indication that the heat has been too great.

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[1] Plattner-Richter, *Hüttenkunde*, p. 6.

The charge for each tube is 5 cwts. of ore, and it takes 3 hours for complete liquation; the yield is 50 per cent. of sulphide. For the production of 100 cwts. of sulphide, 64 cwts. of coal are necessary; the tubes last 20 days each. The cost of producing 100 kilos of sulphide is, for labour, 1·53 francs (=7·4*d.* per cwt.), and for fuel, 1·28 francs (=6*d.* per cwt.); while the cost in pot furnaces is, for labour, 2·21 francs, and for fuel, 6·34 francs per 100 kilos (=10½*d.* and 2*s.* 8*d.* per cwt. respectively).

2. LIQUATION IN REVERBERATORY FURNACES

This method of liquation possesses the merit of being the least expensive in fuel, labour and repairs, but it leads to considerable loss of sulphide by volatilisation. It can, therefore, only be adopted where it is a question of producing large quantities of crude antimony with great rapidity, where fuel is dear, and where the cost of mining the ore is low, and therefore loss of sulphide may be disregarded. It was formerly in use at Ramée in France (la Vendée).

The liquation furnace may be constructed like that for the removal of lead from copper, or like the German refining furnace. In the latter case, a tap-hole must be introduced at the deepest point of the bed. The liquated sulphide will escape through the tap-hole into the receiver placed in front of it. Towards the end of the process the tap-hole is closed, and the furnace strongly fired. The sulphide still in the ore now collects below the layer of slag which forms, and is tapped. The slag is afterwards withdrawn through a side door.

Products of Liquation

These are crude antimony and liquation residues. Crude antimony is frequently contaminated by the presence of arsenic sulphide, lead sulphide and iron sulphide. The extent of this contamination may be seen from the following analyses of sulphides from Hungary:—

	Rosenau.	Liptau.	Magurka.	Neusohl.
FeS	1·102	4·093	—	3·235
PbS	—	—	—	
As_2S_3	0·568	3·403	—	0·247
Cu	—	—	0·59	—
Pb	—	—	3·75	—
Fe	—	—	2·85	—
	1·670	7·496	7·19	3·482

The liquation residues contain upwards of 20 per cent. of sulphide of antimony; it is contained, not only in the interior of the pieces, but also covers them as well, in the form of a thin glaze.

The following analysis shows the composition of these liquation residues[1]:—

Sb_2S_3	20·40
FeS	2·87
FeS_2	1·23
SiO_2	59·84
Al_2O_3	4·65
CaO	5·22
CO_2	4·10
Alkali and carbonaceous matter .	1·69
	100

The liquation residues, when sufficiently rich, are worked up for antimony regulus.

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[1] Hering, in *Dingler*, vol. ccxxx., p. 253.

B. THE TREATMENT OF ANTIMONY-GLANCE AND OTHER ANTIMONY ORES FOR THE EXTRACTION OF METALLIC ANTIMONY.

The treatment of antimony-glance for the extraction of metallic antimony can be done either by the roasting and reduction method or by the so-called precipitation method.

The former consists of an oxidising roasting of the ore, followed by a reduction of the oxide formed during the roasting, by means of coal, with the addition of fluxes and covering materials (soda, potash, glauber salts). The process may be performed in shaft furnaces, reverberatory furnaces, or (in rare instances) in pot furnaces.

The precipitation method is carried out by smelting antimony-glance (or crude antimony) with iron and fluxes. The antimony is separated in the metallic state with formation of sulphide of iron. It may be done in pot, or in reverberatory, furnaces.

The roasting and reduction method is less expensive than the precipitation method, and is suited to the working of poorer ores and liquation residues; it is therefore to be preferred to the precipitation method. The latter is only suited for the smelting of rich ores and of crude antimony, and is more expensive in practice, on account of the high coal consumption and labour cost; it is only rarely adopted.

The antimony ores, other than antimony-glance, are not treated by independent special methods. When sulphuretted, they are worked together with antimony-glance. If they are oxidised ores, they are subjected to a reduction process, *i.e.*, they are mixed with antimony-glance after it has been roasted.

1. THE ROASTING AND REDUCTION PROCESS

This may be resolved into (1) the roasting of antimony-glance and (2) the subsequent reduction of the oxide of antimony formed in roasting.

a. The Roasting of Antimony-Glance

The roasting of antimony-glance can be so conducted that the product shall principally consist of either the stable tetroxide or the volatile trioxide; in the latter case the trioxide would be collected in a suitable arrangement for condensation. The former method of roasting is more usual; the latter, which has been named "volatilising roasting" (*verflüchtigende röstung*), has been suggested for the extraction of antimony, but appears, so far, to have only been adopted for the preparation of the trioxide for use as a pigment.

The chemical changes which take place during the normal oxidising roasting of pulverised antimony-glance, having for its object the conversion of the sulphide into the tetroxide, are the following, if the correct conditions of temperature and air admission are observed:—

When the temperature is raised to the proper point (not much over 350°C.), the atmospheric oxygen converts the antimony trisulphide into sulphur dioxide and antimony trioxide. A part of the latter is further oxidised to the pentoxide, and this, combining with some of the trioxide, forms the tetroxide. Antimonic acid is formed in the presence of oxides of metals, and combines with them to form antimoniates. Furthermore, if the oxides of metals which are inclined to form antimoniates are present, a portion of the trioxide, in the presence of air, and in contact with the foreign oxides, is changed into antimonic acid, and forms antimoniates. No formation of sulphate of antimony takes place. If the ore contains large quantities of foreign sulphides, which on being calcined would form sulphates, antimoniates of the foreign metals are formed instead of the sulphates.

With pure antimony-glance, and the correct temperature and quantity of air, the product of roasting is principally the tetroxide, but it always contains antimony glass and undecomposed sulphide. If there are foreign sulphides and arsenic compounds in the ore, antimoniates, arseniates, and sulphates of the foreign metals are found in the roasted mass.

Since antimony sulphide and antimony trioxide melt at a dark red heat and form antimony glass, and since, furthermore, they are both volatile, the maintenance of the proper temperature is of the greatest importance. According to Bidou it is not allowed to exceed about 350° C.; at lower temperatures the sulphide would not be decomposed. At temperatures only slightly beyond 350°, the mass begins to frit together, thereby preventing the penetration of air to the interior. At still higher temperatures the trioxide volatilises.

By regular rabbling, the fritting of the mass during roasting is prevented even at the higher temperature; and the presence of gangue in the ore also tends to obviate the same difficulty. The richer the ore, the more difficult is it to roast it; with rich ores it is impossible to prevent to some extent both the liquation of a portion of the sulphide and the formation of flue dust, which latter consists almost entirely of antimony trioxide and tetroxide, antimony sulphide, arsenic compounds and carbonaceous matter. It is therefore only possible to raise the temperature for the purpose of oxidising any unaltered sulphide, after the greater part of the sulphide has been converted into tetroxide. Properly roasted ore should appear of a reddish colour while in the furnace, and of an ashy grey colour on cooling; further, while in the furnace it should feel soft under the rabble, and free from any fritting together. If the admission of air during the roasting be limited, the volatile trioxide and not the tetroxide is formed.

The so-called *volatilising roasting*, which is only designed to form and volatilise the trioxide, requires for its execution a restricted air supply and a higher temperature. Steam at a high temperature also effects the formation of the trioxide, with the simultaneous production of sulphuretted hydrogen. This method of roasting was proposed by Hering for the treatment of poor ores and residues from the liquation of crude antimony, but does not appear to have been practically applied. Since the arsenic contained in the ore, when roasted, forms compounds which are more volatile than antimony trioxide, it is possible to separate the two products by intercepting the latter. This method of roasting also has the advantage that the gold and silver, which nearly always exist (with other metals) in these ores, remain in the residue and can be extracted.

The Execution of the Ordinary Roasting

Ordinary roasting (*i.e.*, for the production of the tetroxide) is carried out in reverberatory furnaces which are provided with arrangements for condensation.

Formerly (1862), muffle furnaces were in use in Hungary. The reverberatory furnaces now in use are of two kinds :—

1. *Rabble-furnaces* (intermittent working).
2. *Long-bedded hand-furnaces*[1] (*Fortschaufelungsöfen*).

Rabble-furnaces were formerly in use at Bouc and Septèmes in the department of Rhône in France, and are still used at Siena in Tuscany.

The latter furnaces are used in, among other places, New Brunswick and at Banya in Hungary. They are worked with less cost for fuel and labour than the rabble-furnaces.

The arrangement of the earlier pattern of rabble-furnace with two fireplaces, as used in France, is shown in Figs. 302 and 303.[2]

The horizontal bed *h* is egg-shaped and is 8 feet 3 inches long, with a greatest width of 4 feet 7 inches; *r*, *r* are the two fireplaces, one on each side of the bed, 5 feet 3 inches long and 1 foot 2 inches wide. The gases from the fire pass through the opening F in the roof into the flue and through the latter into the chimney E. A is the working door; S is a hood built above the working door, which draws away the antimonial fumes from the furnace-men.

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[1] See vol. i. p. 68.

[2] Kerl, *Metallurgy*, p. 524.

In these furnaces 5 to 6 cwts. of ground and sifted ore are roasted in 6 hours; during the first 2 hours the working door is closed; after that it is opened, the charge well stirred, and constantly rabbled till the finish. The loss of antimony in properly executed roasting amounts to only 2 per cent.

At Siena[1] 4 cwts. of fine ore are charged at one time, and the roasting requires 3 to 12 hours according to the richness of the ore; ores rich in antimony require a much slower roasting than those which are poor. The consumption of fuel (lignite) per charge is on the average 77 lbs., and the loss of antimony is 5 per cent.

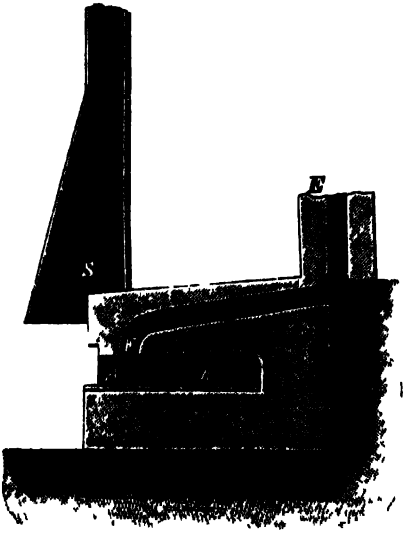

FIG. 302

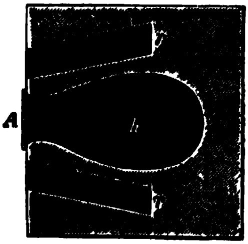

FIG. 303

The *Fortschaufelungsöfen*, used in New Brunswick,[2] is 42 feet 6 inches long, 7 feet 6 inches wide, and has 10 working doors in each side. The height from bed to roof is 2 feet 1 inch, and the firegrate is 2 feet 1 inch wide. The firebridge is 5 feet 2 inches high and 1 foot broad. There are 5 charges of 6 cwts. each in the furnace at one time. During 24 hours, 3 charges (18 cwts.) are drawn, so each charge remains in the furnace 40 hours. During the last 2 hours before being drawn, the ore is strongly heated and rabbled every 5 minutes. Properly roasted ore has a dull, greyish-yellow colour. The consumption of wood is three-quarters of a cord in 24 hours, and the loss of antimony is stated to be 7·5 per cent.

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[1] Bidou, *L'Antimoine en Toscane. Genie civil*, 1882.

[2] *Engineering and Mining Journal*, 1873, vol. xvi., No. 25.

Similar furnaces at Banya are 26 feet 3 inches long, 6 feet 6 inches wide with 5 working doors in one side. Charges of 4 cwt. each are introduced at the end of the furnace farthest from the fire and are drawn after 20 hours; 24 cwts. are roasted in 24 hours. The fuel is lignite, which is burned in a stepped grate.

Furnaces have been proposed with a trough-shaped bed sloping towards one of the longer sides of the furnace, the object being to perform the reduction and roasting in the same furnace. Since the liquation of a certain portion of the sulphide cannot be avoided during the roasting, this arrangement allows it to be tapped off and sent to market as crude antimony.

Volatilising Roasting

This method, as already pointed out, was proposed by Hering for the treatment of poor ores and residues from the manufacture of crude antimony. The ores, or residues, as the case may be, are roasted in a reverberatory furnace at a temperature sufficiently high to volatilise the antimony trioxide, which is collected in condensing chambers; it is said to be very pure and to yield on reduction a very pure metal.

If the oxide is to be used as a pigment, a very limited application of it, it must be of exceptional whiteness, and to ensure this the roasting is conducted in muffles. Oehme obtains this purity of tint by roasting the sulphide in a restricted air supply with admission of steam; this is said to produce an oxide of great purity in white sublimed needles, sulphuretted hydrogen being formed at the same time. The steam is introduced by allowing water to drop into the muffle, and the air enters by a small opening at the front.

The construction of the plant is seen in Figs. 304 and 305.

M is the muffle, *L* is the opening for the admission of air. The water enters the muffle at *w*, flowing along the tube *R* fitted with a cock. The gases and vapours pass out of the muffle through the pipe *x* along the pipe *y* into the condensing chambers *z*, after which they enter the scrubber *s* through the horizontal pipe shown in the figure. The scrubber is supplied with a flow of water which condenses the last portions of trioxide. The incondensible gases pass out of the scrubber along the iron flue *v*; *m* is the firedoor, *n* the door of the ash-pit. After the fire gases have passed round the muffle, they also enter the flue *v*. The chambers are emptied by means of the door *T*.

The supply of water must be regulated so that neither the vapour of trioxide nor the sublimed product are moist, otherwise the sulphuretted hydrogen present would re-convert the oxide into sulphide. Excess of air would lead to the formation of the tetroxide and sulphur dioxide, the former of which would remain in the muffle. A dark red heat is best for obtaining a satisfactory result. The author is not acquainted with the result of working this process.

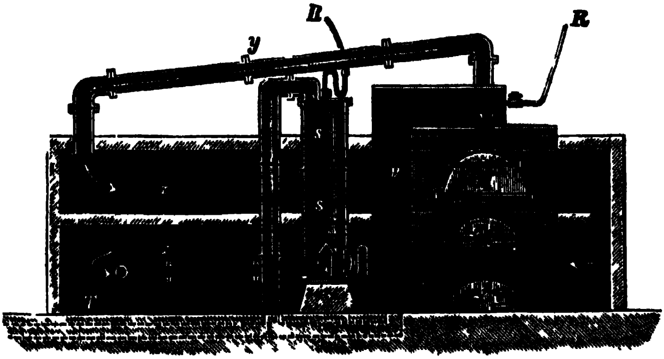

FIG 804.

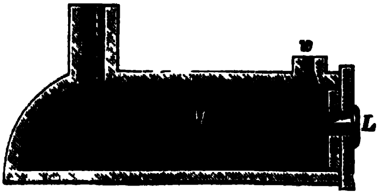

FIG. 805.

b. The Reduction Process

The object of this is to reduce the oxide (either tetroxide or trioxide) to metallic antimony. If coal alone be used for this purpose, a large proportion of the antimony will be lost through volatilisation as trioxide, and any antimony sulphide still remaining in the roasted ore will not be decomposed. Substances are therefore added to the charges which, on account of their easy fusibility, form a protecting cover and prevent the volatilisation of the antimony: these also assist in the formation of fusible slags, and separate the metal from any sulphide of antimony present. The substances which are most advantageous for this purpose are such as remove the impurities from the antimony and also serve as a refining medium. Potash, soda, glauber salt, and other alkaline substances are used.

The reduction is carried out in reverberatory furnaces, in shaft furnaces, and occasionally in crucibles in pot furnaces.

The reverberatory furnace process is simple and easily controlled, but is accompanied by considerable loss of antimony, and is therefore only used where ores are rich and raw fuel cheap.

The shaft furnace method causes less loss of antimony than the former one, and is less expensive, but presents technical difficulties. It is necessary to form a protecting slag which shall be sufficiently thin and fusible to protect the separated antimony from volatilisation and from oxidation by the air blast. It may be employed for ores which are too poor in antimony to be worked in reverberatory furnaces.

Antimony ores are only exceptionally worked in crucibles, as the cost of fuel and labour is very high.

Reduction in Reverberatory Furnaces

The loss of metal with these furnaces is high, amounting at the least to 12 per cent.; indeed Helmhacker says it may rise as high as 30 or 40 per cent. This pattern of furnace is (or was) in use at Bouc, at Septèmes, at Siena, in Upper Hungary, and also in New Brunswick.

At Bouc and Septèmes the roasted ores are worked with oxidised ores from Algiers, and with antimonial flue dust.[1] The furnace-beds are egg-shaped, 7 feet 10 inches long, 5 feet 3 inches wide in the centre, and 3 feet 4 inches wide at the fire-bridge. The bed is a deeply hollow one, built of fire-brick, and slopes from every part to the tap-hole in one of the longer sides. The tapping-pot is placed below the tap-hole, level with the floor of the shed. The height from the bed to the roof in the centre is 3 feet 3 inches. The construction of the furnace is shown in Figs. 306 and 307.

H is the bed, *o* the opening by which the charge is introduced, which is 1 foot 4 inches wide, *x* is the opening through which the charge is worked, *y* is the tapping-pot; *F* is the fire-bridge, the top of which is 1 foot 4 inches above the fire-bars, and 1 foot below the roof, *r* is the fire-place, *p* the roof; *z* is the flue 8 inches in diameter, connected with condensing chambers 400 feet long for the deposition of the antimonial vapour. At the end of the system of condensing chambers is the main chimney. The dust obtained from these chambers contains up to 50 per cent. of antimony. The charge for this furnace consists of 400 to 500 lbs. of roasted ore, oxidised ores and flue dust, 90 to 110 lbs. of a flux consisting of salt, smaller quantities of soda and sometimes a small quantity of glauber salt, 65 to 75 lbs. ground charcoal and 220 to 330 lbs. of slag from the previous charge: this slag contains principally common salt.

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[1] Simonin, *Bull. de la Société de l'Industrie*, vol. ii., bk. 4, p. 577.

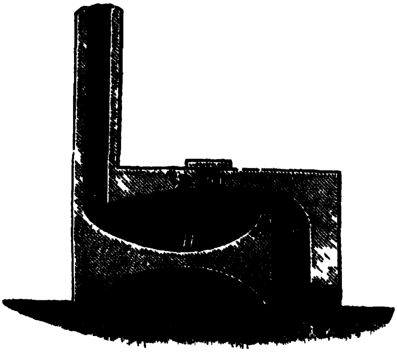

Fig 306

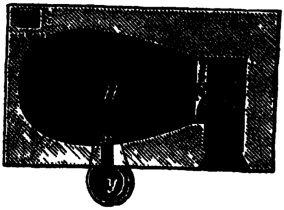

Fig 307

The fluxes are introduced into the furnace first, and fired; when in a state of tranquil fusion, about an hour after charging, the introduction of the other ingredients of the charge is commenced. These are added through the working door in portions of about 44 lbs. at intervals of 15 minutes and well stirred in. After the addition of each portion a scum is produced, which is drawn off through the working door. When the last portion has been added and stirred in, the furnace is strongly fired, and the charge tapped, the whole process occupying from 4 to 6 hours. During the process the antimony is separated from its oxygen and sulphur compounds by the action of the charcoal and soda, gangue is slagged by the soda, and the foreign metals present are carried into the slag as sulphides by the action of the sulphide of soda resulting from the reduction of glauber salt by the charcoal. The salt added to the charge acts, like the glauber salt and soda, as a flux and as a cover, but it also conveys some of the foreign metals into the slag in the condition of chlorides.

The fuel consumption is 5—6 cwts. per charge, and the loss amounts to 14 or 15 per cent. of the total antimony contained in the ore.

The slag and metal collect in the tapping-pot, and after they have become solid are lifted out together, after which the antimony regulus is freed from slag and broken up.

At Siena the procedure resembles that practised formerly at Bouc and Septèmes[1] The following are the figures obtained from the working of 830 charges:—[2]

368,838	lbs	of roasted ore.
268,918	„	„ sea salt
12,641	„	„ soda ash.
88,628	„	„ glauber salt
38,205	„	„ slag from previous charges
4,409	„	„ iron slag.

Antimony obtained 113,573 lbs. The loss of antimony is not given.

In New Brunswick the furnaces are 8 feet 6 inches in diameter, the beds are built of fire-clay and are concave; the depth in the centre is 1 foot 6 inches. The refining follows immediately after the reduction; the roasted ore, 5 cwts. at a time, is spread on the red-hot bed, and covered with 1 cwt. of glauber salt, and 82 lbs. of coarsely powdered hard wood charcoal. After 4 hours the charge is melted and effervescing; the carbonic oxide which is liberated escapes through the layer of slag and burns. The charge is rabbled until it ceases to boil, and then allowed to settle for half an hour. After this the charge is cooled by leaving the fire door open. When the slag has attained a low red heat and is in a pasty condition, it is drawn out, and the materials for refining are added; the furnace is then strongly heated. The added materials are 27·5 lbs. of glauber salt, and 11 lbs. of wood charcoal. Sulphide of soda is formed and produces a slag with the impurities in the antimony. After an hour and a half the metal and slag are in a state of tranquil fusion, and the melted mass is ladled into iron moulds. The pouring is done in such a way that at least half an inch of thick slag remains on the surface of the metal in the mould. In this way it is impossible for the antimony to begin to solidify before the mould is filled. As soon as the ingot is solid, the slag is removed:

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[1] Bidou, *loc cit.*

[2] Knab, *Métallurgie*, p. 528.

it is essentially a sulpho-salt of antimony mixed with sodium carbonate, and contains 15 per cent. of antimony; the latter is recovered by smelting the slag with one-fifth of its weight of iron. Information as to the amount of loss in the process is not published.

In Hungary at one works they are said to combine the refining with the reduction. It is said that 5 cwts. of roasted ore are smelted with 10 per cent. of small coal and 3·6 per cent. of glauber-salt[1] in reverberatory furnaces for 20 hours, the slags are then removed and 22 to 25 lbs. of slag from a previous refining of antimony added. After this is fused, the ladling of the metal is proceeded with.

Reduction in Shaft-Furnaces

This method, as well as the reverberatory furnace method, was practised formerly at Bouc and at Septèmes in France, and at Oakland in California: at the present time it is in use at Banya in Hungary.

At Bouc and Septèmes[2] ores containing 30 to 40 per cent. of antimony were roasted in reverberatory furnaces and smelted in shaft furnaces which were worked on the "*spur*" principle with covered "eye." They were 10 feet 10 inches high, 2 feet 7 inches to 3 feet in depth, and 1 foot 11 inches wide and had three tuyeres. No information is available as to the composition of the charges. In 24 hours 2 to 2½ tons of ore were worked and the coke consumed was half the weight of ore. The crude metal produced contained 92 to 95 per cent. of antimony and was refined.

At Oakland in California, in 1882, oxidised ores were worked in a circular water-jacket furnace. The proportions of ore, etc., in the charge were 80 parts by weight of ore, 100 of slag and 30 of coke. There was no satisfactory arrangement for condensation, and the yield of antimony was only 77⅞ per cent. of the assay value of the ore.

At Banya[3] the materials for the production of antimony were:—

Roasted ore containing	48–49	per cent.	of antimony.
Unroasted oxidised ores	46	„	„
Unroasted liquation residues from the production of crude antimony containing	21·4	„	„
Roasted residues containing . .	23	„	„
Flue-dust	56	„	„
Refinery slag	25	„	,

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[1] *Berg.- und Hütten-Zeitung*, 1862, p. 408.

[2] Simonin, *loc. cit.*

[3] *Stahl und Eisen*, 1886, vol. vi. p. 62.

These are smelted together in shaft furnaces 19 feet 7 [illegible]ches high, the diameter being 4 feet 7 inches at the m[illegible] and 3 feet 4 inches at the tuyere: each furnace has 5 w[illegible] tuyeres and is constructed with a closed crucible; 3,000 cu[illegible]et of wind are supplied per minute at a pressure of 12 inc[illegible] of water. A campaign or "run" lasts 3 weeks. The charg[illegible]re of 2 different compositions A and B below.

		B.
	lbs.	lbs.
Roasted ore	1213	1323
Roasted residues from liquation	1654	1323
Ore moulded into lumps with lime	441	—
Flue dust do. do.	220	—
Unroasted ore	—	220
Oxidised ores	—	220
Unroasted liquation residues	—	220
Limestone	1323	1764
Foul slags from same work	882	882
Slags from refinery	--	441
Impure antimony (III. below)		220

The mixing of lime with the fine ore and flue-dust is only done during the first 8 or 10 days of the campaign, after that time they can be added in their natural state without prejudice to the process. The quantities of lime used at first are, for fine ores, 10 per cent. by weight and for flue-dust 7 per cent.

These 2 charges are used alternately so that 2 charges of mixture A are followed by 1 charge of B, and in 24 hours a total of 30 cwts. is put through the furnace. The unrefined antimony obtained is of 3 grades, of the following compositions:—

	I.	II.	III.
Antimony, per cent.	90·02	73·80	65·04
Iron ,,	6·23	16·66	23·80
Sulphur ,,	2·85	8·42	10·46
	99·10	98·88	99·30
	Per cent.	Per cent	Per cent.
Proportion of total output	82·5	9·0	8·5 = 100

The grades I. and II. are refined: the grade III. is returned to the furnace in the charges as shown above.

The slags produced in this operation have the following composition:—

	I.	II.
SiO_2	46·9	45·9
CaO	34·6	31·4
FeO	15·1	19·9
Sb	0·5	0·9

Slags which are not clean and contain large quantities of antimony are returned to the furnace.

Hering[1] proposed to work the liquation residues of the composition shown on p. 444 in a circular shaft furnace of the following dimensions, height 19 feet 8 inches, diameter at the tuyere level 3 feet 4 inches, number of tuyeres 3, air supply 530 cubic feet per minute at a pressure of 7·8 inches of water. He claimed that in a furnace of this description it would be possible to smelt 7 tons of residues with the addition of 150 per cent. of tap cinder, 40 per cent. of limestone, and 5 per cent. of gypsum or glauber salt, with a coke consumption of 14 per cent. of the weight of the residues.

Reduction in Pot Furnaces

The reduction of roasted ores in crucibles in pot furnaces is, on account of its high cost, only adopted occasionally where a small quantity is required, and where rich ores or crude antimony are available.

The roasted ore is fused with 10 per cent. of its weight of crude argol or with charcoal or anthracite and potash or soda, in fire-clay crucibles heated in a wind furnace or in a galley furnace. The melted metal is cast in iron moulds coated with tallow or thin fire-clay cream.

According to Knab[2] each crucible contains 26·5 lbs. of roasted ore with 10 per cent. of charcoal and 7·15 per cent. of salt or soda. The pots are arranged 10 or 12 in each furnace, and each pot turns out 4 or 5 charges in 24 hours. The consumption of coal is 70 to 80 per cent. of the weight of the ore, and the life of each pot is 7 or 8 charges.

2. THE PRECIPITATION METHOD OF REDUCTION

This method is applicable only to rich ores and crude antimony. It consists in replacing the antimony in the sulphide of antimony by iron, thus separating the antimony in the metallic state, and forming sulphide of iron at a comparatively low temperature. It is impossible, however, to completely separate the sulphide of iron from the antimony, on account of the high specific gravity of the former, and therefore sodium sulphate and carbon are added in order to produce sodium sulphide, which forms with the iron sulphide a fusible slag of low specific gravity which easily separates from the antimony. Common salt is used in England instead of sodium sulphate and carbon. Iron is best used in the form of turnings, shavings, or tin-plate cuttings. In the case of the latter the tin they contain does no harm. The proportion of iron must not be too high in the case of ores containing sulphides of lead and arsenic, because the antimony would not only be contaminated with iron, but also with the lead and arsenic reduced by the iron from their respective compounds.

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[1] *Dingler*, vol. ccxxx., p. 253.

[2] *Metallurgy*, p. 524. Paris, 1891.

With reference to this it must be borne in mind that where sodium sulphate and carbon are used, part of the iron is consumed in decomposing the sodium sulphate. It has been found by experiment that where 10 per cent. of glauber salt and 2 to 3 per cent. of coal are used, 44 per cent. of iron is required; this figure is given by Karsten, but Liebig states that 42 per cent. is sufficient, and Hering uses only 40 per cent. Berthier uses the following proportions:—sulphide of antimony 100, forge scale 60, soda 45 to 50, coal dust 10. The iron in all cases separates out as the monosulphide FeS, or, according to Schweder, as the sulphide Fe_8S_7.

In England it is usual to add excess of iron in order to secure the separation of all the antimony in the ore: this however is only done with ores which are free from lead and arsenic. The excess of iron alloys with the antimony, and is removed by subsequent fusion with more sulphide of antimony.

There is some loss of antimony in the precipitation method owing partly to volatilisation of the sulphide and partly to the fact that the slags carry some away: Karsten states that the yield where crucibles are used is 64 per cent., Berthier 65 to 67 per cent.: the theoretic yield is 71·5 per cent.

This method is carried out, as a general rule, in pot furnaces, but reverberatory furnaces are sometimes used in spite of the inevitable loss of antimony; shaft furnaces have only been applied experimentally; crucible furnaces are adopted in England, Hungary and other places.

In English works, of which the principal ones are:—Messrs. Cookson and Co., Newcastle-on-Tyne, Messrs. Hallet and Fry, Johnson and Matthey, and Pontifex and Wood in London, ores containing 50 to 55 per cent. of antimony are worked.[1] An antimony-iron alloy is first produced by fusing the sulphide in graphite pots with excess of wrought iron. This ensures the extraction of all the antimony contained in the ore. This alloy is then freed from the iron it contains by fusing it in graphite pots with sulphide of antimony, and the metal obtained again fused with suitable materials in graphite pots in order to refine it. All three operations take place in the same furnace. The ore, broken to the size of hazelnuts, is smelted with wrought iron, tin-plate cuttings, salt and slag from the same process, or with skimmings from a subsequent one. Each pot holds a charge consisting of 46·3 lbs. of ore containing 52 per cent. of antimony, 17·6 lbs. of iron, 4·4 lbs. of salt and 1·1 lb. of slag or skimmings. The iron usually consists of 14·3 lbs. of cuttings compressed into a cake and 3·3 lbs. of turnings and borings. The ore, salt, slag or skimmings as the case may be, and the borings are mixed together and placed in the pot, and the cake of cuttings is placed on the top as a cover.

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[1] *Journ. Soc. Chem. Ind.*, Jan., 1892; *English Mining Journal*, March 12, 1892; *The Mineral Industry*, 1892, p. 23.

The furnaces in the largest works each contain 42 pots, which are heated by the flame from two fireplaces, one in each of the short sides of the furnace. In the centre of the roof is a flue which carries away the gases from both fireplaces. The bed of the furnace, including the two fireplaces, is 54 feet long and 7 feet 4 inches wide; the roof is low and in it are 21 openings along each long side, through which the crucibles are put in and taken out. These openings are 14 inches in diameter and are fitted with covers. The sides and roof of the furnace are bound with iron plates, and there are two smaller openings, 4 inches in diameter, in the shorter sides of the roof over the fireplaces for the removal of clinkers, &c.

The two pots nearest the fire at each end of the furnace are charged with antimony for refining.

The smelting of a charge for the production of the antimony-iron alloy takes 3 hours or a little less. When the charge is smelted the contents of the pot are poured into conical moulds and a new charge is introduced. When the contents of the mould are cold the matte and slag are removed from the surface of the antimony by beating it with a hammer, and are thrown away.

The antimony-iron alloy, technically known as "*singles*," contains 91·63 per cent. antimony, 7·23 per cent. iron, 0·82 per cent. sulphur, and 0·32 per cent. insoluble matter.

The iron in the alloy is removed, as already stated, by fusion with sulphide of antimony. To ensure the complete removal of the iron, excess of the sulphide is used. The iron sulphide separates as a matte, and common salt or sometimes soda ash is added as a cover and to flux the sulphides. The charge consists of 92·6 lbs. of broken regulus, 7·5 to 9 lbs. of liquated sulphide, and 4·4 lbs. of salt, and the same furnace is used as in the former process. The fused mass is stirred from time to time with an iron rod, and the time required for a charge is about 1½ hours. At the conclusion of this fusion the slag and matte are removed with an iron spoon and the contents of the pot poured into a conical cast iron mould, the matte and skimmings being added to subsequent smeltings of ore.

The metal which at this stage is known as "*star bowls*" contains 95·53 per cent. antimony, 0·18 per cent. iron, and 0·16 per cent. sulphur. The presence of sulphur, which is due to the excess of sulphide used in the second fusion, may be recognised by the appearance of small glistening patches in the crystalline pattern on the surface of the casting.

In order to remove the sulphur and to produce the so-called "*star antimony*" the "*star bowls*" have to be further refined. To do this a fused mixture of potash and sulphide of antimony is added to the metal in a graphite crucible in the same furnace as was used in the previous operations. The charge is 92·6 lbs. of metal and 8·8 lbs. of the fluxes, the latter being added after the fusion of the metal. The pots are placed in the hottest part of the furnace as close as possible to the fire, and, when the fusion is complete, the contents of the pots are stirred with an iron rod and poured.

The consumption of coal per week for the above method of treatment is 22 tons or 1½ tons per shift of 12 hours. Eleven crucibles are used, on the average, per ton of antimony produced, and 35 men are required to work a furnace, as shown in this table:—

	Per side of the furnace per shift, 12 hours.	For the whole furnace per shift, 12 hours.	Per day of 24 hours.
Firemen	1	—	4
Furnacemen	4	—	16
Refiners	—	2	4
Metal breakers	—	2	4
Charge mixer	—	1	2
Workers on day shift only, viz., one smith, one boiler and engineman, and three labourers	—	—	5
			35

The loss in this process is 10 per cent. of the antimony contained in the ore, the greater part of which is due to volatilisation during smelting. Condensing chambers are connected with these furnaces and are cleaned out four times a year, when a large quantity of white flue-dust is obtained. This contains 70 to 72 per cent. of antimony and is mixed with coal dust and smelted with charges of ore.

At Magurka, in Hungary, the precipitation method was formerly in use: pot furnaces and graphite crucibles were employed. Charges of 20 to 22 lbs. of antimony sulphide with iron, potash, and pan scale (from salt works) were treated. The process was divided into two operations.

Reverberatory furnaces are said to be in use at Linz, Schleiz in Germany, and at Alais in France. It is impossible to prevent considerable loss by volatilisation in these furnaces, and they must therefore be connected with very long condensing flues in order to collect the metallic fume. The bed too must be very tight in order to prevent leakage of the fused metal, which is very fluid. At the deepest point of the bed a tap-hole is provided for drawing off the smelted charge. The detailed results of work in these furnaces are not known to the author; in any case there must be much greater loss than in the pot furnaces.

Hering has experimented with shaft furnaces for the treatment of liquation residues by the precipitation method. Although his experiments were not continued as far as the attainment of a definite result, and in spite of the unsatisfactory results of previous workers, it appears that this method could be carried out in shaft furnaces and that the result would be the more satisfactory the richer were the ores which were treated.

Products of the Extraction of Antimony

These are unrefined antimony and slags. The former contains a series of foreign elements, more particularly arsenic, iron, copper and sulphur, as the following analyses show:—

	1.	2.	3.	4.	5.
Method of extraction	Precipitation.		By reduction of oxidised ores.		From Fahlore-speiss desilverised by amalgamation in the Stephan Works.
Furnace used . . .	Reverberatory.		Shaft furnaces.		—
Analyst	Helmhacker.		—		—
Sb	94·5	84·0	97·2	95·0	90·77
S	2·0	5·0	0·2	0·75	2·0
Fe	3·0	10·0	2·5	4·0	—
Co . . . . Ni	—	—	—	—	1·50
Cu	—	—	—	—	5·73
As	0·25	1·0	0·1	0·25	—
Au	traces	—	—	—	—

The impure antimony has to be refined.

Slags from the extraction of antimony by the roasting and reduction method consist principally of silicates, those from the precipitation method of silicates and sulphides. Some of them are thrown away and some are used in the first smelting of the ores.

THE EXTRACTION OF ANTIMONY FROM METALLURGICAL BYE-PRODUCTS WHICH CONTAIN ANTIMONY

The following bye-products are produced in the process of extracting antimony from its ores: liquation residues, matte, slags, refinery slags and flue dust. These, if sufficiently rich, are added to the charges in smelting the ore; the liquation dross, however, is subjected to a preliminary roasting, and the flue dust is intimately mixed with lime, before it is smelted. Liquation residues are also sometimes treated separately in shaft furnaces.

At the Stephan Works in Upper Hungary, antimony is extracted from the speiss, which has been desilverised by amalgamation; this speiss is obtained by smelting fahl-ores. The antimony is extracted by smelting the speiss with pyritic ores in shaft furnaces. The copper is converted into sulphide by the sulphur of the pyrites, and the impure antimony obtained is refined.

c. *The Refining of Antimony*

Unrefined antimony, as already stated, usually contains sulphur, iron, arsenic and copper, and frequently lead as well. These impurities, with the exception of lead, can be eliminated partly by oxidising and slagging agents, partly by sulphurising agents, and partly by chlorinating agents. Sulphur is removed by fusion with soda or potash or antimony glass (antimony oxysulphide).

Arsenic is converted by soda or potash into arseniate of soda or potash, and can thus be removed. Copper and iron are converted by sulphide of antimony into sulphides; the conversion is facilitated by the addition of soda or potash, or of glauber salt and charcoal. The sulphides of iron and copper form a slag with the sulphide of sodium, which results from the reduction of the glauber salt, and with the soda or potash present. They can also be removed easily by antimony glass.

Common salt, carnallite or magnesium chloride, when added, cause the volatilisation of some foreign metals as chlorides, and slags the others. A large quantity of antimony, however, is volatilised at the same time, so that on the large scale this method is attended with great loss of metal.

The above-mentioned methods do not eliminate lead, because metallic antimony separates lead from its oxide or sulphide; lead can only be separated from antimony by chloridising, which causes great loss of antimony, and even then the lead is only incompletely removed.

Mitscherlich suggested that the lead should be removed from the sulphide of antimony before the latter was smelted, by fusing the sulphide with 4 per cent. of iron; by this means the whole of the lead and a comparatively small amount of antimony would be removed. From all this it is obvious that the best way to produce an antimony free from lead is to use an ore which is itself free from that impurity.

It has already been pointed out that in commerce antimony is judged by the appearance of the fern-like "star" on its surface. This characteristic is not exhibited by impure metal, nor by the pure metal if any part of the surface has been exposed during solidification, nor if the slag covering set before the metal, nor if undecomposed soda or potash come into contact (even in minute quantities) with the surface. Ingots which do not show the star must, if impure, be refined, and if pure, be recast and allowed to cool under the proper conditions. Small ingots will show only a single large star, while larger ones will show several and will have a fern-like pattern on their sides.

The refining is done either in crucibles in pot furnaces, or in reverberatory furnaces. The former method requires a greater fuel consumption, and therefore for the production of large quantities of refined antimony, reverberatory furnaces are preferred, but the loss of metal in the process amounts to between 20 and 30 per cent. At many works in England the refining is performed as a part of the process of extraction.

1. REFINING IN POT FURNACES

This kind of furnace is, or used to be, in use at Septèmes in France, in England, and at Oakland in California.

At Septèmes, 30 crucibles were arranged on a level bed in one furnace; the shape of the furnace being that of a barrel cut lengthways down the middle. The following were the dimensions of the furnace:—length, 7 feet; breadth across each end, 4 feet; breadth in the middle, 5 feet; the bed was 6 inches lower than the bridge. The roof was 8 inches above the bridge, 1 foot 6 inches above the middle of the bed, and 10 inches at the end where the flue left the furnace. The dimensions of the fireplace were:—length, 5 feet; breadth, 1 foot 8 inches; depth from roof to bars, 1 foot 4 inches. The working door was placed in the front longer side and was 20 inches wide. The crucibles were made of fireclay and stood 5 or 6 charges each, each charge consisting of 48·5 lbs. of impure antimony.

The flux used was a mixture of sulphate and carbonate of soda with a little salt and pure oxidised antimony ores; 13 to 17 lbs. of this mixture was added to each charge. The fusion was conducted at a low red heat and lasted 6 hours, during which time 450 to 550 lbs. of coal was used.

In England, the refining is carried out as described on p. 458. The flux used is prepared by fusing together 3 parts of potash and 2 parts of crude antimony; 8·8 lbs. of this is added to 185 lbs. of the impure metal, which must be carefully cleaned from adhering slag and matte. At the conclusion of the fusion, the contents of the pot are poured together into a conical mould; when cold the slag is easily separated from the metal. The slag is used again with the addition of a little potash. The star only appears when the surface of the cooling metal is completely covered with a quarter of an inch of slag. When the ingot is cold the slag is removed by scrubbing with water and sand.

2. REFINING IN REVERBERATORY FURNACES

Reverberatories are or were used at Milleschau, at Banya, at Siena, and at Oakland. It is most necessary that the furnace should have a tight bed and one which will resist the action of the fused alkalies, otherwise the metal will leak through. It is best to build it of blocks of a native fire-resisting stone such as granite; newly cut stone, however, cannot be used, partly weathered and seasoned stone being better.[1] If such stone is not available, a mixture of burnt and raw clay may be used, but in this case it will need to be rammed into an iron pan.

Figs. 308, 309 and 310 show the construction of a furnace built by Hering at Milleschau, and used and worked successfully, and which was particularly commended by Helmhacker.[2]

The bed consists of a granite block *g* which is carried by three iron rollers *c*, in order that it may be easily placed in and removed from the furnace. The rollers run on the three railway bars *f*. The bed is in contact with the furnace wall only at the front, or working side. There is a depression or sump in the bed at *d*, in which the antimony collects and from which it can be ladled; *b* is the working door at the opposite end to the firebridge. On account of the difficulty of working with only one door, the later patterns of furnace are provided with two opposite to each other, one on each side at the flue end of

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[1] *Berg.- und Hutten-Zeitung*, 1883, pp. 1, 44, 145, and 172.

[2] *Berg.- und Hütten-Zeitung*, 1883, *loc. cit.*

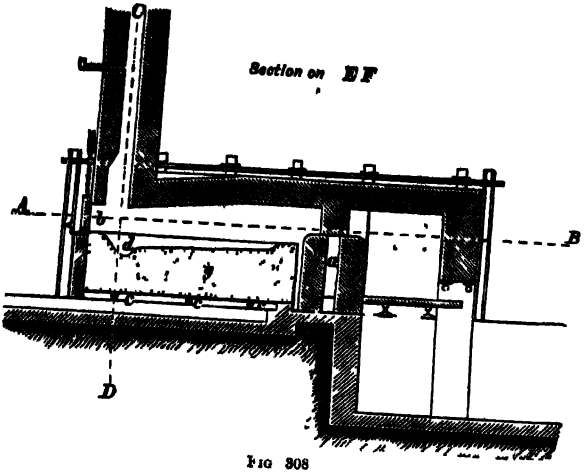
Section on E F

Fig 308

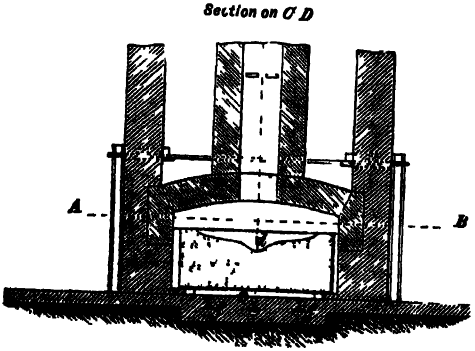
Section on C D

Fig 309

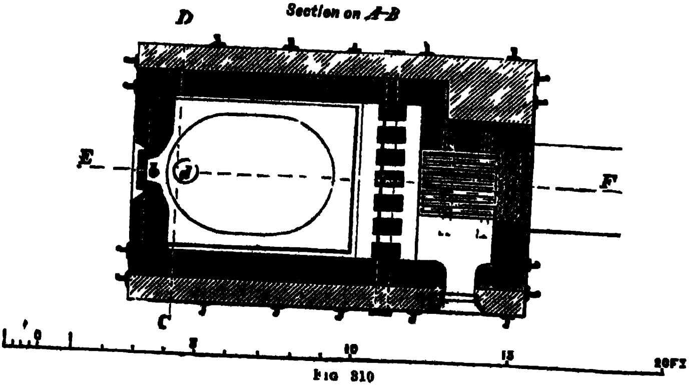
Section on A-B

Fig 310

the furnace. One of them is used to draw the slag, and the other is used for ladling the metal and charging. The firebridge is provided with vertical channels *a*, in which air for the complete combustion of the fire gases can be heated. These channels are connected with a horizontal flue running through the bridge and provided with a slide, so that the amount of air admitted may be regulated. *C* is the chimney provided with a damper. The charge for a furnace of these dimensions is 1,200 to 1,500 lbs. exclusive of the fluxes.

At Banya the bed is built of fireclay 11 inches thick contained by, and well rammed into, an iron box 13 feet long and 8 feet 2 inches wide. A charge consists of 10 cwt. of unrefined metal.

In the Milleschau furnace described above, antimony which contains large quantities of impurity is refined first by soda and then by antimony glass, while the purer sorts are refined by antimony glass alone. The tetroxide of antimony used in making the glass is obtained in the form of crusts which form in the hottest part of the chimney. According to Helmhacker[1] the procedure in refining is as follows:—

The charge of 1,200—1,500 lbs. is thrown into the red hot furnace as rapidly as possible, and melted in less than an hour. Vapour of antimonious and arsenious oxides are given off both during the charging and during the fusion. According to the purity of the metal from 3 to 7 per cent. of soda is added as soon as it is fused; it is well to mix a little coke-dust or fine charcoal with the soda: after this, the heat is raised to bright redness in order to fuse the soda.

The slag gradually becomes thicker and thicker till, after about 3 hours, the bubbles, which at first were numerous, rise very slowly through the charge. The slag is then very carefully skimmed off through the working door.

At this stage iron and sulphur are still left in the metal, and to remove these the materials for the formation of antimony-glass are now added. For each 100 lbs. of antimony in the charge, 3 lbs. of liquated sulphide of antimony and 1½ lbs. of antimony tetroxide are thrown in, and when these are fused 4½ lbs. of potash or white flux are further added.

The fluxes must completely cover the bath of metal.

At the end of a quarter of an hour the antimony is pure and may be ladled, which is done with iron ladles, very cautiously, in order to secure the starred appearance of the ingots. When cold the ingots are removed from the moulds and the layers of slag broken off by means of a hammer.

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[1] *Berg.-und Hütten-Zeitung*, 1883, *loc. cit.*

Three charges of 1,300 to 1,500 lbs. each can be refined in one of these furnaces in twenty-four hours; the consumption of coal is 1,300 lbs. for the three charges.

The slag obtained in the last process of refining, the so-called *star slag*, consists principally of antimony glass, and contains from 20—60 per cent. of antimony; it is generally used over again for refining. When it becomes too impure for this purpose, it is added to charges of ore which are about to be smelted; the other slags obtained in the course of refining are also smelted with ore charges. The impurities in *star slag* are sulphides of iron and nickel, iron oxides and silica.

Loss of metal takes places in refining by volatilisation and in the flue dust, and amounts to 20—30 per cent. Flue dust is principally antimony trioxide and tetroxide. The cost of refining is said to be 2½ to 3 marks per 100 kilos (*i.e.* 1*s.* 3*d.* to 1*s.* 7*d.* per cwt.).

At Banya the charge for the furnace above described is 990 lbs. of higher grade metal (90 per cent. Sb), and 110 lbs. of the lower grade metal (74 per cent. Sb). To this is added 92·6 lbs. of sodium sulphate, 11 lbs. of powdered charcoal and 330 lbs. of raw ore. After 10 hours the slag is drawn off and the materials for forming the star slag are added, viz. :—2·2 lbs. of crude antimony, 13·2lbs. of roasted sulphide of antimony, 7·5 lbs. of potash and 5·7 lbs. of soda ash. The refined star antimony which is obtained contains impurities to the following amounts :—

Arsenic	0·330	per cent.
Iron	0·052	„
Silver	0·006	„
Sulphur	0·720	„
Total impurity	1·108	„

At Siena, where the unrefined metal is less impure, the total weights of 260 charges are given as follows :—115,255 lbs. of unrefined metal, 27,229 lbs. of salt, 767 lbs. of roasted ore, 12,549 lbs. of refinery slag. The refined antimony obtained was 107,697 lbs., which is equal to 93·5 per cent.

The Products of Refining

These are—refined antimony, refinery slag and star slag.

Refined antimony—The composition of metal from different sources is seen from the table on following page.

	I.	II.	III.	IV.	V.	VI.
Source	Lipto Szt Miklos, Hungary.	California.	California.	Samples for tenders at the Royal Docks at Wilhelmshaven.		
Analyst	Hirzel.	Booth, Garret and Blair.	Booth, Garret and Blair.	Himly.	Himly.	Himly.
Sb	98·27	98·34	99·081	98·98	98·81	98·87
Cu	0·54	0·021	0·052	0·01	0·02	0·02
Fe	0·63	0·144	0·039	0·35	0·34	0·16
Pb	—	0·410	0·538	0·34	0·34	0·73
As	—	1·006	0·036	0·09	0·36	0·09
Bi	0·36	—	—	—	—	—
S	—	0·064	0·254	0·23	0·12	0·11
Co and Ni	—	0·013	traces	—	—	—

Refinery slag contains from 20 to 60 per cent. of antimony, and is a mixture of soda, sodium sulphatimoniate, antimony trioxide and tetroxide, ferrous oxide, iron sulphide, arsenic oxide, and smaller proportions of silica and alumina; it is added to charges of ore.

Star slag consists principally of antimony glass, and is used repeatedly till it becomes too impure for further use in refining, when it is added to ore charges.

II. Proposals for the Extraction of Antimony by Wet Methods

There have been several proposals of this nature for the extraction of antimony from poor ores and liquation residues, but as yet they have found no practical application and appear to have no prospect of adoption.

Hydrochloric acid, ferric chloride and alkaline sulphides have been proposed as solvents.

The method of Hargraves,[1] is, to treat the finely powdered ore with hydrochloric acid, heat being applied at the same time. The solution after being neutralised with lime is to be treated with zinc or iron in order to precipitate the antimony. The precipitated metal is to be washed successively with antimony trichloride solution, hydrochloric acid, and water, and then fused with potash in crucibles.

Smith's method is similar.

Hering also proposes hydrochloric acid as a solvent for liquation residues.[2] He precipitates the antimony from the solution as basic chloride, by water, or as sulphide by sulphuretted hydrogen. The latter is to be obtained by digesting the liquation residues with hydrochloric acid. The basic chloride or sulphide obtained is not further treated but is to be sent to market as such.

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[1] *Dingler*, vol. cciii., p. 153.

[2] *Dingler*, vol. ccxxx., p. 253.

Rud. Koepp & Co.[1] propose ferric chloride as a solvent. Sulphide of antimony reduces it according to this equation:—

$$3Fe_2Cl_6 + Sb_2S_3 = 6FeCl_2 + 2SbCl_3 + S_3.$$

E. W. Parnell and J. Simpson[2] have proposed alkaline sulphides as solvents.

III. METHODS PROPOSED FOR EXTRACTING ANTIMONY ELECTROLYTICALLY

Although Classen[3] and Ludwig published in 1885 a method for the electrolytic determination of antimony, no method of extraction based on this principle has hitherto been adopted. It is questionable, apart from the technical difficulties, if antimony can be profitably extracted in this way.

Borchers[4] has proposed a method, based on his own experiments, for the extraction of antimony from ores by the use of insoluble anodes. He uses as solvent sodium sulphide which easily dissolves antimony sulphide, and separates the antimony from the solution by means of the electric current. The action takes place best when three molecules of sodium sulphide (Na_2S) are present for each molecule of antimony sulphide (Sb_2S_3). If the antimony sulphide exceeds this proportion, sulphur is liberated and interferes with the action, while if sodium sulphide be in excess, the resistance of the electrolyte is increased. The strength of the solution should not exceed 9° B. when hot or 12° B. when cold, and to this 3 per cent. of salt is added. The latter promotes the separation of the dissolved sulphide of iron and reduces the electric resistance of the liquid.

Iron tanks are used as decomposition cells, and serve also as cathodes. When the tanks are rectangular iron plates are suspended in the liquid to increase the cathode surface. Lead plates are used as anodes. Lead is not dissolved by the electrolyte in the presence of sulphur compounds; these latter also prevent the formation of large quantities of lead peroxide at the anode as it is reduced at once by the sulphur as soon as formed.

The tension required in each cell for the decomposition is stated to be 2 to 2½ volts, with a current of 3·7 to 4·6 ampères per square foot.

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[1] German Patent, No. 66,547, of 12 April, 1892.

[2] English Patent, No. 11,882, of 1 September, 1884; *Chem. Ztg.*, 1885, p. 412.

[3] *Ber. Deutsch. Chem. Ges.*, vol. xviii., p. 1104; Classen, *Quant. chem. Anal. durch Electrolyse.* Stuttgart, 1886.

[4] *Electro-Metallurgie*, p. 148. Braunschweig, 1891.

Borchers is of opinion that the chemical changes which take place during the electrolysis are probably the following:—

First the current decomposes three molecules of water:—

$$3H_2O = 3H_2 + 3O.$$

At the cathode the following decomposition takes place:—

$$Sb_2S_3 + 3Na_2S + 3H_2 = Sb_2 + 6NaHS;$$

and at the anode the action is represented by the equation:—

$$6NaHS + 3O = 3H_2O + 3Na_2S_2.$$

Other changes also take place during the electrolysis, owing to incomplete circulation in the bath. These minor changes are due to the presence in the bath of sodium hydrosulphide, sodium disulphide and sodium hyposulphite; the presence of all of which in the decomposition products has been quantitatively demonstrated by Borchers. He assumes that oxidation takes place at the contact of the anode with the liquid, before the decomposition products can pass from the cathode over to the anode.

According to the strength of the current, the antimony is deposited either as a black powder or in glistening scales; part of the deposit adheres to the iron and part falls to the bottom of the cell: the former is easily detached with a steel brush. The deposit is washed, dried and fused under antimony glass, yielding a very pure metal. The residual liquor is worked up for the extraction of the sodium hyposulphite contained in it.

As has already been pointed out, the whole success of this method depends on the use of insoluble anodes, and it has not yet been put to the test of use on the large scale.

Borchers has also proposed a plant for the extraction of antimony from ores.[1]

Koepp's method is to act on antimony sulphide with ferric chloride, with the formation of ferrous chloride and antimony trichloride, while sulphur is separated, thus:—

$$2Fe_2Cl_6 + Sb_2S_3 = 4FeCl_2 + Sb_2Cl_4 + S_3.$$

The solution is electrolysed at a temperature of 50° C. between lead plates. The antimony is deposited at the cathode and ferric chloride is formed at the anode. The current used is 3·7 ampères per square foot, but no information is given about the potential in the bath.

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[1] *Electro-Metallurgie*, 1896, p. 337.

Siemens and Halske[1] use as solvent either the sulphides, hydrosulphides or polysulphides of the alkalis. The finely ground ore is lixiviated with a solution of the sulphide or hydrosulphide as the case may be, when the sulphide of antimony is brought into solution in the form of a double salt, *e.g.* with NaHS:—

$$Sb_2S_3 + 6NaHS = Sb_2S_3 \cdot 3Na_2S + 3H_2S.$$

The liquor is then led into the cathode division of a bath which is divided by diaphragms into series of anode and cathode divisions: the former being closed and gas-tight and containing insoluble anodes of carbon or platinum, and the latter being open and fitted with cathodes of copper or antimony plates.

The double salt is decomposed at the cathode, viz.:—

$$Sb_2S_3 \cdot 3Na_2S + 6H = 2Sb + 6NaHS.$$

In this way, in addition to the antimony, there is obtained a liquor which can be used again to dissolve more of the sulphide. Salt or some other alkaline chloride can be added to the solution in the anode cell, whereby chlorine will be liberated. If the lixiviation residues contain gold, silver, copper, mercury, bismuth, zinc, cobalt or nickel, they can be dissolved by means of the chlorine as chlorides and then precipitated by the sulphuretted hydrogen evolved during the lixiviation. If there are none of these metals to be treated in this way the chlorine can be used for other purposes, *e.g.* bleaching.

It is said that this method is applicable both to ores and to metallurgical bye-products, but no practical application appears to have been made of it so far.

Impure antimony which contained gold was for a short time worked up for the extraction of both metals at Lixa near Oporto in Portugal:[2] the process was, however, given up on account of the high working cost. Plates of the impure antimony were used as anodes, the electrolyte being a solution of antimony trichloride. The latter was made by dissolving the trichloride in a concentrated solution of salt, potassium chloride or ammonium chloride strongly acidified with hydrochloric acid. When the current was passed the anodes slowly dissolved, the antimony being deposited on the cathode while the gold in fine powder fell to the bottom of the cell. The material of which the cathode was made is not stated. In spite of the fact that soluble anodes were used, the method proved to be too costly.

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[1] German Patent, No. 67,973, June 29, 1892.

[2] J. H. Vogel, *Zeitschr. für Angewand. Chemie*, 1891, p. 327, and Sanderson. German Patent, No. 54,219, February 26, 1890.

ARSENIC

PHYSICAL PROPERTIES

THIS metal possesses a steel grey colour, and shows a brilliant lustre when freshly broken; it is known in both the crystalline and amorphous conditions. The crystalline form belongs to the hexagonal system, and is isomorphous with tellurium and antimony, while the amorphous form is a dark grey powder which changes into the crystalline modification when heated to 370° C.

The crystalline form can be obtained by collecting the vapour of the metal in a receiver which is only a few degrees colder than the vapour itself; if the difference of temperature be great the amorphous form is deposited. It is also deposited in the amorphous condition when the vapour of arsenic mixed with other gases (*e.g.*, hydrogen or oxides of carbon) is cooled.

The crystalline form is brittle and somewhat hard, but the cast metal flattens slightly under the hammer, although it is easily broken.

The specific gravity of the crystalline variety is 5·727 at 14° C., and its specific heat 0·083 (Wüllner and Bettendorf). The specific gravity of the amorphous variety is 4·71.

Arsenic can be fused at a dark red heat if contained in a sealed glass tube under pressure.[1]

According to Conechy arsenic volatilises at a temperature of 449°—450° C. as a citron yellow vapour which has a strong smell of garlic; it is doubtful if the smell is due to the metal or to some low oxidation product. The vapour, as already pointed out, may be condensed either as crystals or as a dark grey amorphous powder.

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[1] Landolt and Mallet, *Dingler*, vol. ccv. p. 575.

THE CHEMICAL PROPERTIES OF ARSENIC AND ITS COMPOUNDS THAT ARE OF IMPORTANCE IN ITS EXTRACTION

Arsenic does not change in dry air at ordinary temperatures, but in damp air it loses its colour and brilliancy and changes slowly into arsenious oxide. When heated in the air it burns with a bluish-white flame, forming a copious white cloud of arsenious oxide.

Nitric acid oxidises it to arsenious oxide. Aqua regia dissolves it easily, forming a mixture of arsenious and arsenic oxides. Hot concentrated sulphuric acid dissolves it with liberation of sulphur dioxide: the dilute acid does not attack it. Hydrochloric acid attacks it only in presence of air, and then but feebly, with formation of arsenious chloride. Chlorine combines eagerly with it in the cold, forming arsenious chloride. When heated with sulphur it forms sulphide of arsenic.

If arsenic be heated with nitre or chlorate of potassium, an active oxidation of the metal takes place, and potassium arseniate is produced.

OXYGEN COMPOUNDS OF ARSENIC

Arsenic forms two compounds with oxygen, arsenious oxide and arsenic oxide; both of these are acid-forming bodies, and have a much wider technical application than the metal has.

Arsenious Oxide, As_2O_3, *or* As_4O_6

This is also known as arsenious anhydride, arsenic trioxide and white arsenic. It is white, and occurs in both the crystalline and amorphous states.

The crystalline form is dimorphous; it crystallises in the cubic and in the rhombic systems. Octahedra are obtained by cooling a hot aqueous solution of the oxide; a solution in hydrochloric acid gives better results. Rhombic prisms crystallise from a saturated solution in caustic potash. The latter form can also be obtained by heating arsenious acid in closed vessels to a temperature of 300° C.; when left at rest for a long time it slowly changes into the amorphous form.

Amorphous arsenious acid, also known as "arsenic glass," is prepared by subliming the crystalline variety at a high temperature. It is a white transparent mass, which, when left at rest for a long time, changes into the crystalline form, loses its transparency, and assumes a porcelain-like appearance. When arsenious oxide is heated in a closed tube placed in a vertical position, the lower end being at a temperature of 400° C. and the upper at 200° C., the arsenious oxide in the lower part of the tube will be found in the amorphous condition, that in the middle in rhombic prisms, and that at the upper end in octahedra.

The amorphous variety dissolves readily in water and alcohol. The crystalline varieties, however, are only soluble with difficulty in these liquids.

Amorphous arsenious oxide fuses when heated at the ordinary pressure of the atmosphere; the crystalline variety, on the other hand, only fuses under pressure, and solidifies again in the amorphous form.

Arsenious oxide volatilises when heated. The temperature at which it volatilises is given by Wurtz at 200°, by Watt at 218°, by Wormley at 190° C. When a solution of the oxide is evaporated, the oxide volatilises with its solvent between 100°—150° C. Arsenious oxide is reduced when heated with charcoal; the metal volatilises and may be obtained as a brilliant black sublimate.

Arsenious oxide is a powerful reducing agent, and is extensively used on this account as a decoloriser in glass-making, in the manufacture of copper colours, and for the manufacture of yellow arsenic glass.

Arsenious oxide does not combine directly with oxygen, but by the use of strong oxidising agents, such as aqua regia, chlorine, nitre and nitric acid, it can be converted into the higher oxide of arsenic, arsenic oxide. The principal use of arsenious oxide is in preparing arsenic oxide, which is largely employed in the manufacture of aniline dyes.

Arsenic Oxide or Arsenic Anhydride, As_2O_5

This exists both as the anhydride and in combination with water as the corresponding acid. As is the case with the corresponding oxide of phosphorus, arsenic oxide forms three different acids, arsenic acid H_3AsO_4, pyroarsenic acid, $H_4As_2O_7$, and metarsenic acid, $HAsO_3$. These and their salts are isomorphous with the corresponding acids and salts of phosphorus. The pyro- and meta-acids of arsenic, however, are not stable in aqueous solutions as the corresponding acids of phosphorus are; in contact with water they are converted into the ordinary ortho-acid.

The anhydride is a white substance which is only slightly soluble in water, but combines with it if the two are left in contact for a time, forming the acid, which is soluble. At a red heat the anhydride fuses and decomposes into arsenious oxide and oxygen.

Arsenic acid of commerce, H_3AsO_4, is a thick liquid, which, on being heated to the temperature of 180° C., changes into hard, glistening crystals of the pyro-acid, $H_4As_2O_7$, with elimination of water. At a higher temperature, 200°C., more water is eliminated, and the meta-acid $HAsO_3$ is obtained, a white glistening body resembling mother-of-pearl.

SULPHIDES OF ARSENIC

Arsenic forms three sulphides, arsenic disulphide, As_2S_2, arsenic trisulphide, As_2S_3, and arsenic pentasulphide, As_2S_5.

The *disulphide* occurs native as the mineral realgar. A substance of similar composition is manufactured under the name red arsenic glass. This latter substance is used in the preparation of the so-called "Indian fire," and also in tanning, where it is combined with lime for the removal of hair from the hides. It was formerly widely used as a pigment, but latterly has largely gone out of use.

The *trisulphide* is found in nature as the mineral orpiment (auripigmentum). It can be prepared artificially by passing sulphuretted hydrogen through an acidified solution of arsenious oxide. If this sulphide be heated out of contact with air it fuses to a yellowish-red liquid which volatilises without decomposition at the temperature of 700° C. If heated in the air, however, it burns with the production of arsenious oxide and sulphur dioxide. It is insoluble in strong hydrochloric acid, while the sulphides of antimony and tin are soluble. It is soluble in solutions of the caustic alkalis and in solutions of the alkaline carbonates, forming an arsenite and a sulpharsenite of the alkali metal, *e.g.*:—

$$2As_2S_3+4KOH=KAsO_2+3KAsS_2+2H_2O.$$

Arsenic trisulphide is again precipitated from this solution on adding an acid.

This sulphide of arsenic was formerly highly esteemed as a pigment in oil painting, but has of late years been replaced by chrome yellow and picric acid. It is chiefly used now in the same way as realgar is.

Arsenic pentasulphide is prepared either by fusing together the trisulphide and sulphur, or by treating sodium sulpharseniate, Na_3AsS_4, with an acid. The latter salt is obtained by acting on the trisulphide with polysulphide of sodium.

HYDRIDES OF ARSENIC

There are two of these compounds, gaseous arseniuretted hydrogen, AsH_3, and solid arseniuretted hydrogen, As_4H_2. The former, which is extremely poisonous, is prepared by generating hydrogen in a solution which contains arsenic; the latter is a brown solid body, and is prepared by acting on pure sodium arsenide with water.

CHLORIDE OF ARSENIC

is produced when powdered arsenic is burned in chlorine gas, or by distilling arsenious oxide with hydrochloric acid. It is an oily colourless liquid which, when exposed to the air, evaporates in white, highly poisonous vapours.

COMBINATIONS OF ARSENIC WITH OTHER METALS

Arsenic combines with certain metals forming bodies known as speiss. These only faintly resemble alloys, being much more closely allied to the compounds of metals with the non-metallic elements.[1]

ORES OF ARSENIC

Arsenic and its technically important compounds are extracted from nickel and cobalt ores as well as from specific ores of arsenic. Among the latter, *native arsenic*, *mispickel*, and *leucopyrite* are the most important. The other arsenic minerals, *arsenic bloom*, *realgar* and *orpiment*, occur but seldom, and do not form the subject of special processes for the preparation of arsenical products, but are worked up with other ores of arsenic.

Native Arsenic

Native arsenic, also known as *flaky arsenic*, usually contains small quantities of iron, cobalt, nickel, antimony, silver and frequently also gold. It usually occurs in association with silver, lead, cobalt and nickel ores, and is found at Freiberg, St. Andreasberg, Kapnik in Hungary, Kongsberg in Norway, at St. Marie-aux-Mines and at Allemont in France, and in Cornwall.

Mispickel,

$FeS_2 + FeAs_2$, *arsenopyrite*, or *arsenical pyrites*, contains arsenic, 46·1 per cent., sulphur, 19·6 per cent., and iron, 34·3 per cent. The iron is sometimes replaced to the extent of from 6 to 9 per cent. by cobalt, in which case it constitutes a cobalt ore. It also contains sometimes small quantities of gold and silver. It is the most widely distributed ore of arsenic, occurring in the Erzgebirge, Silesia (at

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[1] Schnabel, *Allgem. Hüttenkunde*, p. 10.

Reichenstein), Hungary, Styria, England (Cornwall and Devon), Sweden, France (Puy de Dome and Haute Loire), Canada, etc. It is accompanied by silver, nickel, cobalt, tin, lead and copper ores as well as by pyrites.

Arsenide of iron

occurs massive as *löllingite* and crystallised as *leucopyrite*. *Löllingite* (Fe_2As_3) contains 66·8 per cent. arsenic, while leucopyrite ($FeAs_2$) contains 72·84 per cent. These frequently contain small quantities of gold, as at Ribas in Spain, and at Reichenstein in Silesia. At the former place the leucopyrite, according to Güttler, contains from 14 to 16 dwt. of gold per ton.

This mineral occurs less copiously than mispickel, and is found at Silesia, Reichenstein, Bohemia, Styria, Schladming, Carinthia (Lölling, near Hüstenberg). It is usually found in association with the same ores as mispickel.

The rare minerals—*arsenic bloom*, *arsenite*, or *arsenolite*, As_2O_3, *realgar*, As_2S_2, and *orpiment*, As_2S_3, are of no importance as sources of arsenic.

Among the arsenical cobalt and nickel ores must be mentioned *cobalt glance*, *tin-white cobalt* or *smaltine*, *skutterudite*, *white arsenical nickel*, *red arsenical nickel*.

In addition to the above sources of arsenical products, ores of tin, silver, lead and copper, which contain mispickel or leucopyrite, produce considerable quantities as bye-products.

THE METALLURGICAL EXTRACTION OF ARSENIC AND ITS COMPOUNDS

In addition to metallic arsenic, which has comparatively small technical importance, arsenious oxide, sulphide of arsenic, and mixtures of these are prepared in metallur[illegible] works. The quantity of these arsenic compounds used in the [illegible] very considerable.

Dry methods are used for the working of ores and metallurgical products, but wet methods have been proposed for the recovery of arsenical compounds from residues from the manufacture of the aniline colours. The electrolytic method has been proposed for the extraction of arsenic from its sulphide, but so far has not been [illegible]t into practice.

We have therefore to distinguish between:—

I. The extraction of arsenical compounds from ores [illegible]allurgical products.

II. Methods proposed for the recovery of arsenical compounds from coal-tar colour residues.

I. THE EXTRACTION OF ARSENICAL COMPOUNDS FROM ORES AND METALLURGICAL PRODUCTS

Here we must further differentiate into :—

1. The extraction of arsenic.
2. The extraction of arsenious acid.
3. The preparation of vitreous realgar.
4. The preparation of vitreous orpiment.

1. THE EXTRACTION OF ARSENIC

A. *Extraction by the Dry Method*

Almost the only dry method of extracting arsenic is that of heating mispickel or leucopyrite in the absence of air. Formerly another method was employed, viz., by the reduction of arsenious acid by means of carbon. This method is, however, now abandoned, because a very large proportion of the arsenic prepared by it was obtained in the amorphous condition.

When mispickel is distilled the arsenic is driven off and can be collected. The following equation shows theoretically the chemical change which takes place :—

$$2(FeAs_2FeS_2) = As_4 + 4FeS\ ;$$

but in actual working a very considerable quantity of the arsenic, amounting in some cases to a half, remains behind in the residue.

Leucopyrite, when distilled, parts with a portion of its arsenic, and leaves behind a lower arsenide of iron as shown by this equation :—

$$16FeAs_2 = 7As_4 + 4Fe_4As.$$

In practice, however, the residue is richer in arsenic than it should be theoretically.

To prevent waste of the arsenic in the residues from the above processes, they are roasted in a reverberatory furnace, and the arsenious oxide which is formed, is collected.

As the arsenic is only wanted in the crystalline form, the sublimation must be conducted with the greatest care and the receivers must be maintained at the correct temperature.

The formation of more or less of the amorphous pulverulent arsenic cannot in any case be prevented; and it is used for the preparation of arsenical compounds.

The distillation is performed in pot furnaces built of fire-clay, Tubes or pots are arranged in two rows, one on each long side of a fireplace in a galley furnace. Where pots are used, several rows can be arranged one above the other. To the front of the pots, cylindrical receivers of fire-clay are attached. These are provided on their front side with doors of sheet iron, by opening which the progress of the sublimation can be observed towards the end of the process. The joint between the sublimation vessel and the receiver must be properly luted, and the door on the receiver must be made tight with clay. In order to prevent loss by volatilisation during the working, the tubes themselves are glazed externally. They are 5 to 7 inches in diameter and 2 feet 4 inches long. The charge in each tube is several pounds of mispickel. Sheet iron rolled into a spiral is placed in the mouth of each tube so that it projects 4 inches into the receiver and 4 inches into the tube. This assists the formation of crystals of arsenic in the shape of glistening grey scales.

After the tubes or jars are charged, the spiral of sheet iron is placed in position, and the fire started: the receivers are not put on until arsenic vapour begins to appear. The process is complete when no more arsenic vapour is seen on opening the doors of the receiver. When mispickel is treated in the way described above, sulphide of arsenic is volatilised at the beginning of the process and collects in the receiver (Freiberg). The addition of potash or caustic lime prevents the sublimation of sulphide. The time required for the process varies, according to the amount of arsenic in the ore, from 8 to 12 hours, where charges of several pounds per tube are used. After the completion of the process the receivers are taken away, and the sublimation residues are removed.

Crystalline arsenic collects on the iron spiral in the mouth of the tube, while the larger portion of that which collects in the cooler parts of the receiver, is amorphous. The spirals are cautiously unrolled to remove the scales of arsenic which have been deposited. These scales possess a particularly bright lustre, and are fit for sale without further treatment; they lose their brilliancy after a very short time, in consequence of the formation of a thin film of arsenic suboxide, but, according to Boettger, this film can be easily removed by a boiling hot solution of potassium bichromate to which a little sulphuric acid has been added.

At Freiberg, ores containing[1] 76 per cent. of mispickel (*i.e.* 35 per cent. of arsenic) are worked in galley furnaces, in which there are 26 tubes in two rows on each side, 6 in the upper, and 7 in the lower row. The charge of ore for the whole furnace is 7 cwt. and the extraction requires 10 or 12 hours. The product is 165 lbs. of arsenic from the spiral of sheet iron, and 27 lbs. of sulphide of arsenic out of the receivers. The residues, which are argentiferous, retain 3 per cent. of arsenic. They are added to a furnace charge in smelting for silver-lead in order to extract their silver. The sulphide which collects in the receivers is used for the preparation of vitreous realgar.

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[1] *Preuss. Zeitschr.*, vol. xviii., p. 189.

At Reichenstein,[1] in Silesia, arsenic is extracted from mispickel. The furnace formerly used contained 26 glazed tubes, each 2 feet to 2 feet 6 inches long and about 5 inches wide, and the charge was 5 cwt. of mispickel in the form of slimes. The product consisted of 90 per cent. of crystalline, and 10 per cent. of amorphous arsenic: the residues which retained one-third of the arsenic originally present in the ore, were worked up for the production of arsenious acid.

At Ribas[2] in Spain, arsenic used formerly to be extracted. There were 22 tubes per furnace, each 2 feet 4 inches long, and about 7 inches in diameter: 8 to 10 cwt. were charged at a time, and the process lasted 9 hours. In this time 200 pieces of peat and 2·7 to 3·9 cubic yards of coal were consumed. The arsenic obtained was used in the manufacture of shot.

B. *The Electro-Metallurgical Extraction of Arsenic*

Siemens and Halske[3] have proposed this method for the extraction of arsenic from those ores and intermediate products which contain the sulphide. By treatment of the ores with sulphides, hydro-sulphides or polysulphides of the alkali metals, the arsenic is brought into solution as a double salt, and the latter is subjected to electrolysis. Sodium hydro-sulphide gives a solution according to the equation:—

$$As_2S_3 + 6NaHS = As_2S_3.3Na_2S + 3H_2S.$$

Similar soluble salts are produced by the hydro-sulphides of potassium and ammonium. The arsenic is separated from these solutions in the manner described for antimony on page 470. The following equation shows the change which takes place when the arsenic is precipitated by the current:—

$$As_2S_3 3Na_2S + 3H_2 = As_2 + 6NaHS,$$

and similarly for the double salts formed with potassium and ammonium respectively. In the anode division of the bath alkaline chlorides are decomposed, the chlorine evolved being utilised in order to bring into solution as chlorides the metals contained in the ore residues, or, if there are none present, for the preparation of bleaching powder. There has been so far no application of these methods, and the prospect of their introduction is very small, because the suitable ores of arsenic are leucopyrite and mispickel, from which arsenic cannot be directly extracted as sulphide.

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[1] Kerl, *Metallurgy*, p. 506.

[2] *Berg.- und Hütten-Zeitung*, 1853, p. 764.

[3] German Patent, No. 67,973, June 29, 1892.

2. THE MANUFACTURE OF ARSENIOUS OXIDE

Arsenious oxide is produced by the roasting of special ores of arsenic or of those ores of gold, silver, nickel, cobalt, lead, copper and tin, which contain arsenic.

The special ores of arsenic are mispickel, leucopyrite and native arsenic; the others, particularly the ores of tin, copper and gold, usually contain large quantities of these arsenic compounds, especially mispickel.

By far the largest quantity of arsenious oxide produced at the present time comes from Cornwall and Devon, where it is extracted from mispickel, either pure, or mixed with ores of copper and tin. The following are the principal mines:—Botallack, Levant, East Pool, South Crofty, Tin-croft, Wheal Agar, Callington United, Danescombe and Drakewells in Cornwall, and Devon Great Consols and Gawton in Devonshire.

The process adopted for the extraction of arsenious oxide is to drive off the arsenic in the ore as arsenious oxide by roasting, and to collect the latter in chambers and flues; in most cases the flue dust contains impurities and needs to be purified by sublimation. Sublimed arsenious oxide is either crystalline, or in the form of white powder: the latter form, sometimes obtained by grinding the crystals, is most frequently met with in trade; some however is found in the form of lumps, the so-called *arsenic glass*, *vitreous arsenic* or *white glass*. It is prepared by subjecting the purified arsenious oxide to a further sublimation at a higher temperature.

We must therefore distinguish between:—

A. The extraction of crude arsenious oxide.

B. The purification of crude arsenious oxide.

C. The preparation of vitreous arsenic.

A. *The Manufacture of Crude Arsenious Oxide*

Arsenical pyrites, mispickel and native arsenic, either alone or mixed with other ores, are the special sources of arsenious oxide.

The changes which occur when these are roasted are the following:—

Leucopyrite ($FeAs_2$) At a dull red heat, arsenic vapour is given off, being followed by arsenious oxide as the temperature rises. The iron is nearly all converted into ferric oxide, but a small proportion is converted into ferric arseniate.

Mispickel (FeS_2+FeAs_2). Below red heat it evolves arsenic sulphide vapour. At higher temperatures it is converted into a mixture of ferric oxide, ferric sulphate and ferric arseniate, sulphurous acid and arsenious oxide being at the same time liberated

Native arsenic is changed into arsenious oxide.

The operation of roasting takes place either in muffle furnaces or in reverberatory furnaces. In the former the fuel consumption is higher, but on the other hand neither ore dust nor small particles of coal nor soot get mixed with the arsenious oxide. The latter would be a serious matter, as during the sublimation the arsenious oxide would be reduced by the carbonaceous matter to metallic arsenic.

In reverberatory furnaces this difficulty is best avoided by the use of gas as fuel.

The furnaces must be connected to condensing chambers and flues, suitably constructed for the recovery of the arsenious oxide. The flues or chambers are best built on a level for convenience of emptying. With muffle furnaces it is important to have sufficient cooling in the flues in order to maintain the draught and to prevent the formation of large crystals of arsenious oxide. The best material to use for the flues is sheet lead, over which water can be allowed to trickle in case of need. The so-called "poison-towers," which were tower-shaped erections with flues, one above the other, have gone out of use on account of the excessive draught and the difficulty of cleaning them out.

The construction of a muffle furnace such as was formerly in use at Reichenstein in Silesia is shown in Fig. 311, in which *b* is the muffle, of which the bed is 11 feet 3 inches long and 7 feet 2 inches broad; *c* is the fire-place: the fire gases travel through 5 channels *l* below the bed towards the cross flue *e*, and through them into the flues *f*, one on each side of the furnace and on to the forked chimney *g*. The arsenious oxide liberated in the muffle passes along the flue *d* into a system of condensing flues not shown in the figure; the air required to oxidise the charge enters at the opening *i*. The small chimney *h* serves to carry off the fumes which escape at the working door *z*. The residues in the muffle were drawn into the chamber *t* after the removal of the slide *k*, and *a* is a hole in the roof through which the ore is introduced on to the bed.

At St. Andreasberg in the Harz, cast-iron muffles, 7 feet 6 inches long, 1 foot 7 inches wide, and 1 foot 2 inches high, were formerly employed.

At Freiberg, reverberatory furnaces with a single bed and two working doors on each side are used; they are heated by producer gas made from gas coke: the beds are 15 feet long and 10 feet 10 inches wide.

In Cornwall and Devonshire the arsenical ores are roasted in hand-worked long-bedded reverberatory furnaces, or in Brunton's rotary calciner, or Oxland's rotating cylinder furnace.

The long-bedded reverberatory furnace has working doors on one only of the long sides, the other long side being also the long side of a contiguous furnace. These double furnaces measure over all 24 feet long and 16 feet wide, and the dividing wall is 1 foot 6 inches thick. The inside measurements of a single furnace are:—length 20 feet, width 6 feet 3 inches, and the maximum height of the roof above the bed 1 foot 4 inches. The fire-place for each furnace is 4 feet long and 2 feet wide, and the top of the fire-bridge is 9 inches above the surface of the bed. There are 5, or sometimes 6 working doors, and the ore is introduced through a hopper at the end farthest from the fire and spread towards the bridge.

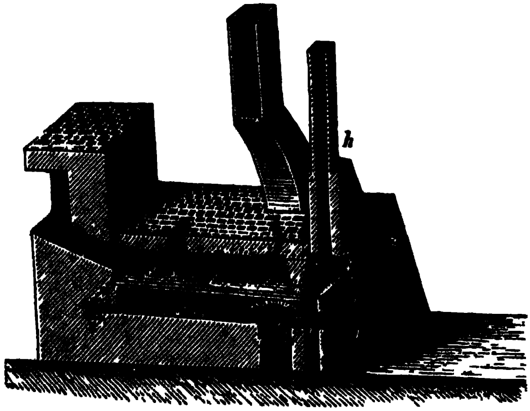

Fig 311

Brunton's calciner is arranged as shown in Figs. 312 and 313. *a* is the bed fixed to a vertical shaft, *b* is the fire-place, *c* is the hopper through which the ore is introduced into the furnace. A fixed rake *f*, which stirs up the ore as the bed *a* revolves, causes the ore to travel gradually from the centre to the circumference where it escapes through the shoot *g* into one of the chambers *h*, *h*, according to the position of the valve *z*. The flue connecting the furnace with the chimney *v* is not shown in the figure. The diameter of the bed is from 12 to 16 feet, and it makes from 5 to 10 revolutions per minute.

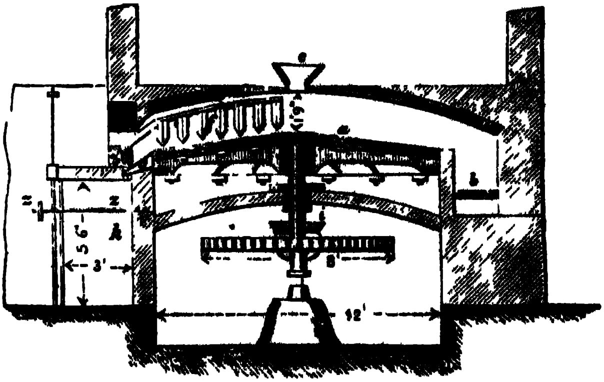

Fig. 312

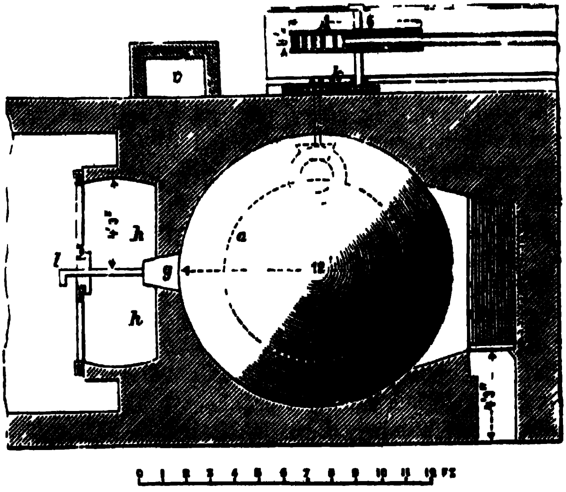

Fig. 313.

The Oxland furnace is shown in Figs. 282 and 283 on page 389.

The length of the inclined cylinder is 23 to 30 feet, and it is lined with firebrick and provided with longitudinal ribs; its diameter is about 5 feet. The power required for one furnace is about 2 to 3 horse power. This pattern of furnace requires less fuel and labour than the long-bedded furnace or Brunton's calciner, but the cost of repairs is greater and it is more difficult to maintain in it an even temperature and a regular draught. In consequence of the strong draught fine particles of ore are drawn into the flues and deposited with the arsenious oxide.

At Deloro, in Canada,[1] mispickel which contained gold was formerly worked. The ore contained 42 per cent. of arsenic and 20 per cent. of sulphur. The furnace used consisted of two cylinders of the Oxland type one above the other. Instead of the longitudinal rows of projecting ribs, there were 4 walls extending from the axis of the cylinder to the circumference, thus dividing it into four entirely separate portions. In the upper half of the furnace the ore remained in one of these four portions of the cylinder; but in the lower half of the cylinder the division walls were provided with slits so that the ore could fall from one of the four divisions into that next to it, thus coming into intimate contact with the air. The air was drawn out by an exhauster placed near the chimney.

The length of the upper cylinder was 29 feet 6 inches and its diameter 5 feet 6 inches, and it was connected by a tube with the lower cylinder 59 feet long and 6 feet 6 inches diameter, and was worked by natural draught. It contained division walls, like the upper cylinder, extending from the lower end to a distance of 4 feet from the upper end, but for the remaining distance it was provided with ribs; these, however, were not placed longitudinally but spirally. The greater portion of the arsenic was driven off in the upper cylinder. The arsenious oxide which was collected in the condensing chambers was re-sublimed in reverberatory furnaces.

All the furnaces are connected with a set of flues or chambers in which the volatilised arsenious oxide is condensed as flue-dust. These are built of either masonry or sheet lead. It was proposed for pure ores to use chambers built of sheet iron suitably protected from rusting.[2]

Pure arsenious oxide in the form of a fine powder is said to be deposited in these chambers as the result of roasting pure ores.

Fig. 314 shows the ground plan of a condensing flue for arsenious acid; *v* is the furnace, *k* is the flue, zig-zag in plan, and opening into the dust chamber z. The gases on leaving the chamber z, pass through a second chamber y into the chimney E. The greatest portion of the arsenious acid is deposited at the bends of the flue. The flue walls near the furnace are built of masonry, but after a certain distance from the furnace sheet lead is the best material.

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[1] *The Mineral Industry*, 1893, p. 34.

[2] *Ibid.*, p. 35.

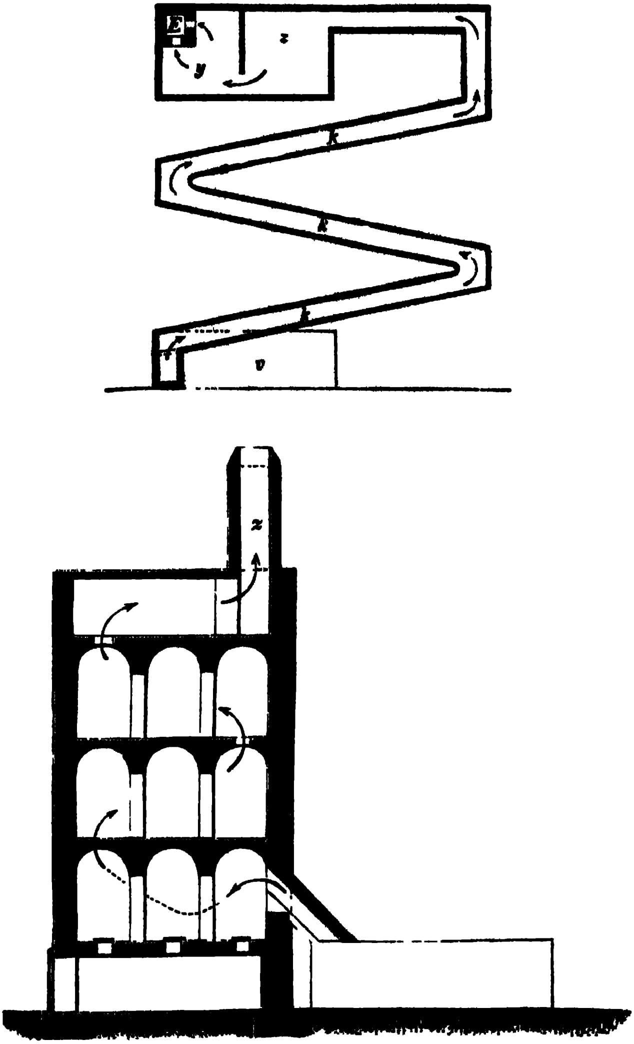

FIG. 315.

The construction of the tower-condenser or "poison-tower," which was formerly used, is shown in Fig. 315. Chambers were built alongside each other in sets, one set above the other, and the stream of furnace gases, after passing through one set of chambers, went on to the set next above, till at the end it entered the chimney *z* placed on the top.

This arrangement is not efficacious for cooling the gases, it is expensive in construction, and is difficult to clean. This latter objection is of importance on account of the poisonous nature of the arsenious oxide: it is therefore no longer used.

In Cornwall and Devonshire the arsenic is condensed in zig-zag flues built of masonry, and connected with the furnace by straight flues 100 to 200 feet in length. They are 5 feet to 5 feet 6 inches high, 3 feet to 3 feet 6 inches wide, and in one case more than 1,000 feet long. Those gases which are not condensed pass, by a flue 200 feet long, into a chimney 60 to 120 feet high. At Gawton, the total length of flue between the furnace and chimney is about an English mile.

In working any description of furnace, it is important to observe that neither ore dust nor carbonaceous matters are allowed to get into the arsenious oxide; the latter would, when the arsenious acid is sublimed, reduce some of it to metal. It is therefore necessary to shut off the condensing arrangement from the furnace when the latter is being charged or emptied, and also when the charge is being rabbled or stirred. At these times the furnace is temporarily put into communication with a secondary chimney. The temperature should be only high enough to volatilise the arsenic, and the charge should be cautiously rabbled from time to time. When the charge ceases to give out any flame, the roasting is complete, and the charge is removed by gradually withdrawing it at the bridge. The time required for a charge depends on the amount of arsenic, iron and sulphur contained in the ore. The arsenious oxide is removed periodically from the flues and chambers.

In the muffle furnaces at Reichenstein in Silesia, which have been described above, 8 to 10 cwts. of arsenical pyrites, in the form of slimes, are roasted in a charge about 4 inches deep; the time required is 12 hours, and the coal consumed is 7 per cent. of the weight of the raw ore. The residue contains from 3 to 5 per cent. of arsenic, and is treated by Plattner's chlorine process for the recovery of the gold which it contains. The white arsenic collected in the condensers is either sold as such, or converted into arsenic-glass.

At St. Andreasberg in the Harz, native arsenic containing 65 per cent. arsenic, 4·5 per cent. lead, and 0·5 per cent. silver, was formerly worked in the cast-iron muffles already mentioned. The charges of 4 to 6 cwts. required 22 hours and the fuel (beechwood) consumed was 22 cubic feet. The arsenic obtained was all converted into vitreous arsenic. The residue amounted to 50 to 52 per cent. of the weight of the ore, and contained 1 to 2 per cent. of silver, and 12 to 16 per cent. of arsenic; it was treated to extract its silver.

At Ribas in Spain[1] charges of 20 cwt. used to be worked in muffle furnaces. They required 24 hours and consumed 4 cwts. of coal. In a reverberatory furnace with gas fuel 3 tons of ore were roasted in 24 hours with 4 cwts. of coke.

At Freiberg[2] arsenious oxide is produced from ores containing lead and comparatively little arsenic (12 per cent. or less); dust containing arsenic from the flues of the other roasting furnaces is also used. Gas-fired furnaces are used as previously described, and coke is used as fuel, so as to get a flame free from soot. Each furnace is connected with a flue 820 feet long, for condensation. The charges vary according to the proportion of arsenic present, from 12 to 22 cwts., and the roasting lasts 5 to 8 hours. The residues, containing 1·5 to 2 per cent. of lead, are used for the extraction of that metal. The arsenious oxide of a grey colour, deposited in the nearer portions of the condensing flue, is purified by re-sublimation; the other portions are either sold as white arsenic or converted into arsenic glass.

In Cornwall and Devon 8 to 10 tons of ore are roasted in 24 hours, the coal used being 3 cwts. per ton of roasted ore. The furnaces have been described on page 482. Six men are required for each double furnace, working 8-hour shifts.

In the Brunton calciner described on page 483, 4 to 5 tons of ore are roasted in 24 hours: the tables make 5 to 10 revolutions in the hour, and the coal used is 1½ to 2 cwts. per ton of raw ore; 2 men working 12 hours each are sufficient to work the furnace during 24 hours.

In the Oxland furnace described on page 389, 20 to 25 tons of ore are roasted in 24 hours: the ores contain 15 per cent. of arsenic and require 1 cwt. of coal per ton of ore roasted: 3 men and 3 boys working 8 hours each are sufficient for the working of these furnaces per 24 hours.

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[1] *Berg. und Hütten. Zeitung*, 1853, p. 767.

[2] *Pr. Zeitschr.*, vol. xviii., p. 189.

B. *The Refining of the Crude Arsenious Oxide*

In most cases it is necessary to purify the arsenious acid from foreign matter by resublimation: none but the purest ores yield at once marketable white arsenic. The commoner impurities are:—grains of ore, volatile constituents of the ores, flue dust and carbonaceous matter. Reverberatory furnaces with either gas or solid fuel are used, the former being preferable, as the arsenic produced in them is free from soot, ash-dust or cinders. Condensation chambers or flues are attached to the furnaces to collect the arsenious acid.

At Freiberg, where comparatively impure flue-dust is worked, the gas-fired furnace previously described (page 482) is used for the production of white arsenic. Charges of 12 cwt. are heated for 8 hours and yield 85 per cent. of their arsenic; the residues are worked up for lead: 10 to 12 cwts. of coke are used every 24 hours.

In Cornwall and Devon, where the crude arsenic contains about 70 per cent. of the oxide, furnaces similar to those used for roasting the ore, page 482, are used.

Each pair of furnaces, having one long side in common, form one double furnace, the length and breadth being each 16 feet: each furnace has 3 working doors in its long side and the greatest height of the roof over the bed is 1½ feet. The fuel used consists of a mixture of coke and anthracite in equal quantities, and the gases and vapours leaving the furnace pass along a flue 100 feet long into a series of 12 chambers arranged in a zig-zag manner, each chamber being 7 feet high, 14 feet long and 4 feet wide, the total length of passage being 167 feet. From the chambers the gases pass into the chimney.

The foreign matter which accompanies the vapour is deposited in the flue leading to the chambers, whilst, in the latter, the arsenic condenses in crystals; these are ground in a mill like a flour mill and packed in wooden barrels.

C. *The Production of White Arsenic Glass*

White arsenic glass or vitreous arsenic is prepared by collecting the vaporised arsenic at a temperature so high that the sublimate fuses together into a mass.

There are two methods of procedure, *Glasmachen* and *Gröbemachen*. The former, *Glasmachen*, is used when it is desired to change pure arsenious oxide into the vitreous form, the latter, *Gröbemachen*, when it is desired to purify the arsenious oxide first.

The plant is the same in both cases, and consists of cast-iron retorts heated by an open fire and attached to cylindrical receivers [illegible] wrought or cast iron. The retorts must be made of cast iron [illegible] free as possible from graphite; otherwise the carbon will reduce the arsenious oxide to suboxide of arsenic, and this will give the sublimate a grey colour.

The sublimed oxide collects on the walls of the receiver, at the top of the receiver is a sheet-iron hood connected by a sheet-iron tube with a condensing chamber in which any uncondensed arsenious oxide collects.

Figs. 316 and 317 show the arrangement of the plant *B* is the fireplace, 3 feet wide, in which is suspended the retort *a*, 2 feet 5 inches deep, 2 feet in diameter and capable of holding a charge of 2½ cwt. of white arsenic. The wrought-iron receivers *b*, *b*, each in three sections, rest on the retorts, and are provided with handles. The joints are luted with a mixture of loam, hair and blood. At the upper end of the receiver is the leaden hood *c*, connected with the chamber *f* through the tube *e*.

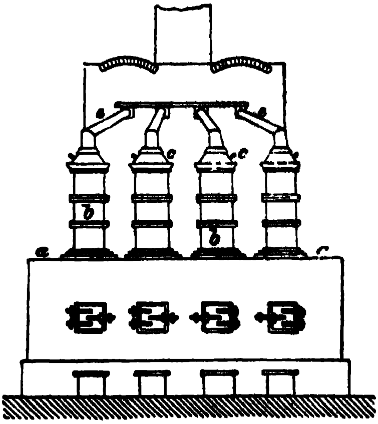

Fig 316

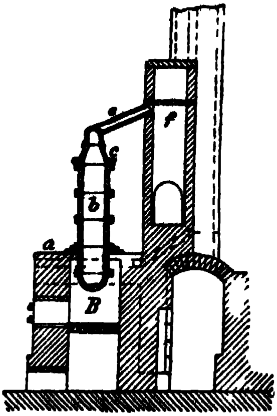

Fig 317

When the *Gröbemachen* process is employed to purify the arsenious oxide before its conversion into the vitreous form, it is necessary to regulate the temperature so that there shall be no sintering of the charge in the retort; otherwise the sintered oxide would not sublime over. When the correct temperature is employed the greater portion of the arsenic is obtained as a bulky, light sublimate on the walls of the receiver. The portions which escape through the receiver are condensed in the chamber beyond. The process is known to be ended when an iron bar, inserted through an opening in the hood, is no longer covered with a white deposit: the opening is closed by a tight-fitting door. When this point is reached, the fire is allowed to die out, and the sublimate removed to be converted into vitreous arsenic by the *Glasmachen* or "running" process.

The residue in the retort is returned to the ore-roasting furnaces. If it is desired to produce an impure arsenic-glass direct from an impure arsenious oxide, the temperature must be raised so high that the sublimate in the receiver fuses together. The product obtained in this way is known as crude arsenic-glass. It is of a grey colour, on account of the impurities in the arsenious oxide having passed over with it, and requires a further sublimation if white vitreous arsenic is to be made from it. The grey colour may be produced either by metallic arsenic, or by fine ore dust in the arsenious oxide employed.

For the *Glasmachen* or preparation of pure vitreous arsenic, the same apparatus is employed. The fire is urged to such a degree that the walls of the receiver are hot enough to fuse the sublimed arsenious oxide to a glass. If the temperature should be allowed to get too high, the amount of sublimed arsenic which passes into the chambers beyond the receiver is excessive; if it should not be high enough, the sublimate is powdery and loses its translucency. When the receiver is at the correct temperature, water hisses when sprinkled on the upper portion from a bunch of twigs, and instantly evaporates from the lower portion. The end of this process is tested in the way described above. The charges are 2½ to 3 cwt. each, and require 8 to 12 hours. At the end of the process the furnace is allowed to cool for 14 to 16 hours, and the vitreous arsenic is removed from the walls of the receivers, which it covers as a scale to a depth of from 1 to 2 inches.

The product is the amorphous modification of arsenious acid, and when freshly prepared is transparent and glistening with a conchoidal fracture. After long exposure to the air it passes into the crystalline form and resembles porcelain, with a waxy lustre.

At St. Andreasberg in the Oberhartz,[1] crude arsenious oxide was formerly worked in charges of 2½ cwt. into a crude arsenic-glass, and the latter converted in charges of 3½ cwt. into pure vitreous arsenic. Each sublimation took 8 to 12 hours, and yielded 89 per cent. of vitreous arsenic and 7 per cent. of residue, of which 40 to 60 per

[1] Kerl, *Metallhüttenkunde*, p. 513.

cent. was arsenious oxide. The 4 per cent. of apparent loss was partly actual loss and partly due to the powdery arsenic formed.

The consumption of wood fuel was 12 cubic feet per cwt. of glass produced.

At Ribas, in Spain, charges of 4 cwt. of purified white arsenic were worked in 7 hours; the fuel consumed was 150 lbs. wood and 74 lbs. coal per charge, and the glass obtained was 96 per cent.

At Freiberg the charges consist of 2½ to 3 cwts. each. The fuel consumed is 2 to 3 cubic feet per charge, and the time 8 to 12 hours; 87·5 per cent. of glass is obtained. The retorts used are about 23 inches in diameter and about 19 inches deep. The receivers are in three sections of about 23 inches diameter and a total height of about 38 inches. The top of the cover which closes the upper end of the receiver is 5½ inches in diameter, and is connected to a tube of the same diameter which leads into the condensing chamber. The life of a retort is about 150 charges.

3. The Production of Red Arsenic Glass or Realgar

Realgar (also known as *ruby sulphur*, *arsenrubin*, *rauschroth*, *sandarach*, etc.) is a combination of arsenic and sulphur which approaches in composition to native realgar. In colour it varies from rose to hyacinth red with an orange yellow streak. It is manufactured by subliming a mixture of mispickel and iron pyrites, or one of mispickel and sulphur. Both methods yield the same product, the two constituents being expelled by the heat and combining in the state of vapour.

If sulphur and arsenic be merely fused together, compounds are obtained which do not possess the desired colour; neither does the fusion of arsenic trioxide with sulphur yield realgar of the desired quality.

It is not essential, in order to obtain a good product, that the sulphur and arsenic should be employed in the correct molecular proportions. The best proportions for a product of any particular shade are discovered by trial.

The process consists of two distinct parts. The sublimation yields a product (*rohglas*) of unreliable composition which is brought up to the desired shade by further fusion with sulphur or arsenic. We shall therefore describe :—

A. The production of *rohglas*.

B. The conversion of *rohglas* into realgar or the "refining" of *rohglas*.

A. *The Production of "Rohglas"*

The sublimation is carried out in a retort furnace. Usually the mispickel is mixed with an equal weight of iron pyrites. At Freiberg a mixture of the desired composition results from the preliminary mechanical dressing of the ores, whilst at other places it has to be specially prepared..

The furnace used at Freiberg contains 12 retorts in 3 rows; each retort is 4½ feet long, about 5 inches diameter, and 0·7 inch thick in the walls, and each is protected from contact with the flame by empty retorts placed under them. These latter are known as *protecteurs.* Each furnace has two fireplaces. The charge is introduced at the rear of the retort, which is afterwards closed by a tile. The front end of the retort opens into a receiver fitted to it. This receiver is a sheet-iron box fitted with an opening for the escape of the steam liberated during the process; the progress of the operation can be watched through it.

At Freiberg the charge of iron and arsenical pyrites contains 10 to 15 per cent. of arsenic and 30 to 35 per cent. of sulphur, and a small quantity of silver, which is extracted from the residue after sublimation. A charge weighs about 60 lbs. and occupies only two-thirds of the retort.

The retort, when charged, is heated to redness for from 8 to 12 hours, after which the residue is drawn out. The residues still contain 0·5 per cent. of arsenic and 23 to 24 per cent. of sulphur, and are, after being roasted, added to a smelting charge for silver-lead. The receivers, which contain *rohglas* in both the compact and pulverulent form, are emptied after each third charge. The massive *rohglas* is treated by the refining process, while the pulverulent product is added to a subsequent charge to be again sublimed. Each furnace treats from 12 to 14 cwts. of ore in 24 hours with a consumption of 8 to 10 cwts. of coal; 6 furnaces are worked by each gang of 4 men working 8-hour shifts.

At Reichenstein[1] it was formerly the custom to work charges of 5 cwt. of arsenical pyrites and 87 lbs. of crude sulphur in glazed earthenware retorts, such as were used for the production of arsenic; each charge was worked off in 6 to 7 hours, and the yield was 168 lbs. of *rohglas* per charge.

At Ribas[2] equal parts of mispickel and iron pyrites used to be sublimed in clay retorts. Each charge was 8 cwts. and yielded

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[1] Fresenius, *Zeitschrift*, 1871, p. 308

[2] *Berg. und Hutten Zeitung*, 1858, p. 774.

1½ cwts. of *rohglas*, the fuel used per charge was 2 cwt. wood and 3 cwt. coal, and the time required was 6 to 7 hours.

B. *The "Refining" of "Rohglas"*

The first process is usually conducted so as to produce a *rohglas* which shall be relatively rich in arsenic and poor in sulphur; and therefore, to bring it to the right shade, sulphur, as a rule, has to be added in the second process. It rarely happens that the opposite course is resorted to.

The refining is carried out in pans or pots of cast iron, provided with a discharge pipe at the bottom. The *rohglas* is rapidly fused in these by quick firing, and then stirred. Impurities form a slag on the surface, known as refinery slag, and these are skimmed off and the requisite quantity of sulphur or arsenic, as the case may be, is stirred in with an iron bar.

As soon as the fused material runs freely from the iron bar and shows on cooling the requisite colour and compactness, the newly-formed slag is skimmed off and the refined realgar is run into conical, air-tight, covered moulds made of sheet iron. When cool, it is broken into pieces and at once ground to fine powder. The slag is used for the production of white arsenic.

At Freiberg, the pans used are 16½ inches in diameter and 23 inches deep, and the charge consists of 3 cwt. of *rohglas* and 40 to 60 lbs. of sulphur. The process occupies 1 to 2 hours, and the product contains 75 per cent. arsenic and 25 per cent. of sulphur. Chilian mills are used for grinding.

At Reichenstein,[1] the charge used to be 4 cwt. of *rohglas* with 30 per cent. of sulphur, which produced 479 lbs. of realgar.

At Ribas,[2] charges of 4 cwt. *rohglas* were refined in iron pans in 2 hours each, by the addition of 45 to 56 lbs. of sulphur.

4. THE PRODUCTION OF ORPIMENT

This pigment, also known as *rauschgelb* and *auripigment* (corrupted into *orpiment*), consists of arsenious oxide coloured yellow by arsenic sulphide. It is really not the same in composition as the mineral known by the same name (As_2S_3).

It is manufactured by subliming together arsenious oxide and sulphur, the proportion of the latter being determined by the shade required. The apparatus employed is that described above for the production of vitreous arsenic, the temperature of working being high enough to keep the sublimed orpiment liquid till the apparatus cools.

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[1] Fresenius, *loc. cit.*

[2] *Loc. cit.*

At Freiberg the process is as follows:—4·5 to 9 lbs. of sulphur are placed in the bottom of the retort, and 280 lbs. of white arsenic are placed on top of it; the mass is heated till an iron wire plunged in the melt is no longer coated when drawn out. During the process a portion of the arsenious oxide is reduced to arsenic by part of the sulphur present, sulphur dioxide being liberated. The reduced arsenic and the rest of the sulphur combine to form sulphide of arsenic, which is always contaminated with small quantities of free sulphur. The lowest receiver contains adhering to the walls, a fused mass of orpiment, varying in colour from citron yellow to orange red; the other receivers contain an irregular streaky product, which must be fused. A certain quantity of powdery product is also obtained which is added to subsequent charges for resublimation.

The charge of the above composition will yield seven-eighths of its total weight of orpiment in the solid or pulverulent form.

At Reichenstein, white arsenic with the addition of 5 per cent. of its weight of sulphur was formerly used for the preparation of orpiment.

Buchner[1] gives the following proportions of sulphur in different varieties of orpiment:—

	%S	corresponding to %As_2S_3
1. Very transparent, streaky	2·5	6·4
2. Twice refined, deep colour	1·05	2·68
3. Moderately strongly coloured . .	1·34	3·43

All these samples contained part of the sulphur uncombined, a small residue being left on treatment with ammonia.

When sulphuric acid which contains arsenic is purified by treatment with sulphuretted hydrogen, a sulphide of arsenic is obtained which corresponds in composition to the mineral orpiment: this method however is not well suited for the production of the pigment. When this precipitate was washed and heated in an iron retort in an atmosphere of coal gas the sublimate was an unsightly, dark-coloured glass which contained organic matter. At Freiberg it is usual to work this product (from the purification of oil of vitriol by sulphuretted hydrogen) after drying it, by burning it in the kilns for the production of sulphur dioxide for sulphuric acid manufacture, the arsenic being obtained as arsenious acid.

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[1] *Berg. und Hütten-Zeitung*, 1871, p. 245.

II. THE EXTRACTION OF ARSENICAL PRODUCTS FROM THE RESIDUES FROM THE MANUFACTURE OF COAL-TAR COLOURS.

For this purpose a large number of methods have been proposed. The arsenic is principally in the form of arsenite or arseniate of lime, and the products aimed at are usually the two free acids. Most of the proposals depend on reducing the arsenic compound to the metallic state at a red heat by organic matter and burning the metallic vapour in air to form arsenious acid.

Winkler's Method.[1]—The mother liquors from the magenta crystals are treated with soda in excess, in order to form arseniate of soda. The liquid is then evaporated in pans till crystals appear on its surface, after which it is mixed in boxes with powdered limestone and coal dust, and well stirred to form a solid mass: for every 100 lbs. of sodium arseniate in the liquid, 30 lbs. of limestone and 25 lbs. of coal are added. In the next process the limestone and coal together decompose the sodium arseniate; it is said that coal alone would not effect it The mixture is next heated in a muffle with a double bottom. On the upper bed the water is driven off, and the dry mixture, when put on the lower one and heated to a red heat, gives off arsenic vapour, while sodium carbonate and lime remain behind. The arsenic vapour passes into condensing chambers where, meeting a current of air, it burns to arsenious oxide and is deposited. The sodium carbonate is extracted from the residue by solution and used again for the preliminary saturation: the lime also can be used again.

Rando & Co.'s, and Tambourin & Lemaire's Methods.—The aniline residues are washed, dried and heated to redness with coke, the reduced arsenic which is liberated in the state of vapour is burned, and the arsenious oxide collected in chambers.

Bolley's Method.—The residues are heated with hydrochloric acid or with salt and sulphuric acid. Arsenious chloride is given off and collected in water, when the greater part of the arsenic is precipitated as arsenious acid.

Stopp's Method.—The residues are digested with hydrochloric acid in order to dissolve all the arsenic, the solution is then saturated with soda, and the arsenic is precipitated by adding lime. The precipitate is treated with sulphuric and nitric acids which convert the lime into insoluble gypsum, while the arsenic as arsenic acid remains in solution.

The author is not in a position to state how far any of these methods are in actual practice.

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[1] *Deutsche Industrie-Zeitung*, 1876, p. 333, and *Verh. d. Vereins zur Beförderung des Gewerbfl.*, 1876, part 3, p. 211.

NICKEL

PHYSICAL PROPERTIES

NICKEL possesses an almost silvery white lustre with a steel-grey tinge, and great brilliancy.

The specific gravity of cast nickel is 8·35; of rolled nickel between 8·6 and 8·9.

With great hardness and capacity for taking polish it combines great malleability: it can be easily hammered, rolled, or drawn into wire. Sheets 0·0008 inch thick and wire 0·0004 inch in diameter may be made from it.

The tensile strength of nickel surpasses that of iron. According to Deville, a wire made from nickel containing 0·3 per cent. silicon and 0·1 per cent. copper bears a strain of 200 lbs., whereas a similar wire of iron breaks under 133 lbs. Kollmann examined a specimen of nickel from the manufactory of Fleitmann in Iserlohn, containing $\frac{1}{20}$ per cent. magnesium, and found that its absolute tensile strength and extensibility were equal to that of Bessemer steel of medium hardness. The breaking strain is 87,110 lbs. per square inch, with an elongation of 15 to 21 per cent., and the elastic limit is 55,170 lbs. per square inch.

Nickel is attracted by a magnet, and then becomes magnetic itself: it loses this property at 350° C.

Nickel can not only be welded to itself at a white heat, but it can also be welded to iron and certain alloys. Fleitmann is the inventor of the method of manufacturing nickel-plated wares by an application of this property. He welds iron and steel to pure nickel or to a nickel-iron alloy, and also welds nickel to alloys of copper and nickel. The method adopted is either hammering or rolling. For such welding to be successful, the necessary condition is the complete exclusion of air from the surfaces to be welded, which Fleitmann attains by various methods.

The coefficient of expansion of nickel between 0° and 100° C. is 0·001286 according to Fizeau; its specific heat is 0·1108.

Nickel is difficultly fusible. According to older experiments it melts at about 1600° C.; the newer work of Schertel gives it between 1392° C. and 1420° C. According to Knut Styffe[1] its melting point is about 1450° C. It is more readily fusible if it contains carbon.

Molten nickel has the property of absorbing carbon monoxide and giving it out again on cooling. The alloys of nickel with copper also possess this property in a degree which increases directly with the percentage of nickel, and the temperature of the fused metal. Further, if certain substances (carbon and various oxides) are present in molten nickel, carbon monoxide is generated by action between them at certain temperatures. The occluded gas makes the nickel porous, and unsuitable for hammering and rolling. In order to obtain nickel free from blowholes, it is necessary to observe special precautions, to be described in the proper place.

Commercial nickel is exceedingly impure, being contaminated by substances of which even traces affect its valuable properties. The most harmful impurities are arsenic, sulphur, oxide of nickel and chlorine.

0·1 per cent. of arsenic makes nickel brittle, and incapable of being rolled.

0·1 per cent. of sulphur renders nickel unsuitable for rolling. It appears, from the results of experiments at the Berndorf Nickel Works at Vienna, that the same proportion of sulphur in alloys like German silver, is harmless.

Iron in German silver lessens its extensibility and destroys this property altogether when the proportion of iron in the nickel used amounts to 1 per cent.

Nickel alloys containing much iron are especially remarkable for tenacity and strength, as was discovered in 1890. Nickel has the power of increasing the strength and elastic limit of iron. These alloys are used for armour plates and artillery. The proportion of nickel in them is from 3 to 27 per cent. The amount of carbon is about 0·06 per cent.; the amount in the alloys used in making nickel steel 0·4 per cent.

Copper gives to nickel a yellow or brownish-red hue, but exerts no injurious influence on its properties as long as its proportion is less than 1½ times that of the nickel.

Cobalt increases the whiteness of nickel, and, up to a proportion of 6 per cent., has no influence on its tensile strength. A greater proportion is said to make the nickel brittle.

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[1] *Oesterr. Zeitschr.* 1894, p. 340.

Carbon is dissolved by molten nickel, and seems not to affect its good qualities, as long as oxides are not present at the same time. It makes nickel slightly more fusible, but also brittle under certain conditions. According to Jungk[1] the separation of carbon in the form of graphite from molten nickel takes place readily if the nickel contains a large proportion of cobalt. Carbon may be separated from nickel by silicon in the same way as it is separated from iron. According to Gard, commercial nickel may contain the greater part of its carbon in the separated form of graphitic scales. A sample of nickel produced by him, with 2·1 per cent. carbon (of which 2·03 per cent. existed as graphite) proved to be strongly magnetic, soft, and tolerably ductile. By passing marsh-gas over nickel he increased the proportion of carbon to 12 per cent., and this carbon seemed to be in chemical combination. Boussingault obtained, at a high temperature in a cementation furnace, a specimen of nickel, which held the same proportion of carbon as very hard steel, but all the essential properties of the original metal were retained. It therefore appears that nickel, unlike iron, is not hardened by the increase of its carbon. Nevertheless alloys of iron which are rich in nickel can be made harder by increasing their proportion of carbon (nickel-steel). According to Fleitmann nickel absorbs cyanogen, which makes it short.

According to Ledebur nickel absorbs its own monoxide, and this injures its tenacity and malleability, as cuprous oxide does that of copper. He also states that the percentage of oxygen (existing as monoxide) in brittle non-ductile cast nickel is 0·304; while in ductile nickel it is 0·084, and in cast German silver 0·061.

Ledebur also states that when nickel monoxide and carbon are both present in the metal, carbon monoxide is produced on fusion, and renders the castings unsound.

Nickel takes up silicon as iron does, when it is reduced from the oxide by carbon at a very high temperature in the presence of silica. Gard found in such nickel about 9·5 per cent. carbon, and 6·19 per cent. silicon. Nickel containing silicon has the physical properties of grey cast-iron.

Phosphorus, in the proportion of less than 0·3 per cent., exerts no injurious influence on the qualities of the metal. Above this proportion it makes it harder, and decreases its malleability.

Chlorine may be present to the extent of 0·18 per cent. in nickel separated in the wet way, and makes the German silver, for which this metal is used, unfit for rolling.

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[1] *Dingler*, vol. 222, p. 94; vol. 236, p. 480.

CHEMICAL PROPERTIES

Nickel is pyrophoric when reduced from its oxide by hydrogen at a comparatively low temperature. When prepared in other ways it is unaltered in either dry or moist air at the ordinary temperature. The quantity of carbon dioxide present exerts no influence. Heated in the air, it first assumes rainbow colours like steel does, and becomes covered, at a red heat, with a greenish grey deposit of nickel monoxide, which is changed by strong heating into dull-green nickelo-nickelic oxide (hammer scale). In oxygen it burns as iron does, forming the monoxide.

Nickel at a red heat decomposes steam very slowly, as the metal becomes covered with olive-green crystals of the monoxide.

It is only very little acted on by hydrochloric or sulphuric acids, in the cold. Dilute nitric acid and aqua regia dissolve it readily; concentrated nitric acid makes it "passive" like iron. This is supposed to be due to the formation of a coat of nickelo-nickelic oxide. Fused alkalis attack nickel but slightly; it is therefore used in laboratories for crucibles.

CHEMICAL REACTIONS OF NICKEL COMPOUNDS WHICH ARE OF IMPORTANCE IN ITS METALLURGY

OXIDES

There are two oxides of nickel, and each forms a corresponding hydrate.

Nickelous Oxide, NiO,

or nickel monoxide, has a green colour. It is formed when nickel is heated in oxygen, in air, or in steam, as well as when nickel sulphide or arsenide is roasted; also by heating nickelous hydrate or sulphate.

At a strong red heat this oxide is reduced to metal by carbon or by carbon monoxide, the metal not melting. At the temperature of 230° C., the powdered oxide is reduced to metal by hydrogen; and as before said, metal thus prepared is pyrophoric. In mixtures of nickelous and ferrous oxide, the nickel is first reduced by coal or carbon monoxide.

With silica this oxide combines to form silicates.

Whereas when cuprous oxide and copper sulphide are heated together in proper proportion, the whole of the metal is separated and sulphur dioxide evolved, the heating of nickelous oxide with nickel sulphide produces no reaction.

If this oxide is heated with iron sulphide or arsenide, we get ferrous oxide and nickel sulphide or arsenide. In presence of silica the iron oxide will form a silicate.

Nickelous oxide and copper sulphide do not react.

It dissolves in acids, forming nickelous salts.

Nickelous Hydrate, $Ni(OH)_2$,

is precipitated from solutions of nickel salts, by hydrates of the alkalis and alkaline earths. It is a bright green powder, converted by heating into the monoxide; all the nickel salts are derived from the monoxide.

Nickelic Oxide, Ni_2O_3,

or nickel sesquioxide, is black. It is obtained by gently heating nickelous carbonate or nitrate. Like the monoxide, it can be reduced to metal; and again like it, it does not react with the sulphide. No salts corresponding to it are known.

It dissolves in sulphuric and nitric acids, forming nickelous salts, and setting free oxygen; in hydrochloric acid it forms nickelous chloride and sets chlorine free; it also dissolves in ammonia with the separation of nitrogen.

The *hydrate* of this oxide is obtained by treating nickelous hydrate, suspended in water, with chlorine.

NICKEL MONOSULPHIDE

is found native as *millerite* or *nickel pyrites* (*hair-pyrites*). It is obtained as a brittle bronze-yellow mass by heating nickel with sulphur; or as a powder, mixed with metallic nickel, by heating the sulphate strongly with coal, carbon monoxide or hydrogen.

The hydrated sulphide can be obtained as a brownish-black precipitate by the action of alkaline sulphides on nickel salts. This is difficultly soluble in dilute hydrochloric acid. Small quantities dissolve in excess of the alkaline sulphide, imparting to it a brown colour.

Nickel sulphide is decomposed by copper, with the separation of metallic nickel, according to the following equations:—

$$NiS + 2Cu = Cu_2S + Ni$$
$$2NiS + 2Cu = Cu_2S + NiS + Ni.$$

When the sulphide is roasted, part of the sulphur passes off as dioxide, and the nickel is oxidised. A portion of the sulphur dioxide formed produces sulphuric acid, and forms nickel sulphate. Strong heating changes this last into nickelous oxide and sulphur trioxide (or sulphur dioxide and oxygen). By sufficiently long continued roasting at the proper temperature, nickelous oxide alone may be obtained; otherwise there will be a mixture of the oxide, the sulphate and unaltered sulphide.

If compounds, or mixtures, of nickel and iron sulphides are carefully roasted, a mixture of nickel monoxide and ferric oxide is obtained. As sulphate of nickel is a very stable compound, the roasting can be so conducted, if a sufficient quantity of sulphur be present, that the greater part of the nickel is obtained as sulphate, and the iron as ferric oxide. If the roasting is interrupted before all the sulphur is removed, a mixture of oxides, sulphates and sulphides of nickel and iron will remain.

By roasting nickel and copper sulphides in the same way, it is possible to get nickel monoxide and cupric oxide; or a mixture of oxides and sulphates as above mentioned. Again, as nickel sulphate is stable at a higher temperature than copper sulphate is, it is possible, with a sufficient proportion of sulphur in the ore, to conduct the roasting so that nickel remains chiefly as sulphate, and the copper as oxide.

If the three sulphides are used together, the same is true. Nickel may be obtained as sulphate, instead of as monoxide, while the other two metals appear as ferric and cupric oxides.

If a mixture of the oxides and sulphides of iron and nickel is heated with coal and silica, nickel sulphide and ferrous silicate are formed, if the proper proportion of sulphur is present; but if there is more sulphur present than can combine with the nickel, a mixture of ferrous and nickel sulphides is produced: this is known as nickel matte.

Similarly, if the mixture contains oxides and sulphides of the three metals, iron, copper and nickel, and if the correct proportion of sulphur be present, it is possible to regulate the fusion so that sulphides of nickel and copper, and ferrous silicate shall be obtained; if, however, there is too much sulphur present to produce that result, a nickel-copper matte is produced, which will contain the sulphides of all three metals.

If a stream of air under pressure is passed through molten nickel matte containing silica, the iron combines with the latter, and sulphur dioxide is liberated, while the nickel sulphide is not affected.

If a current of air be passed through the remaining nickel sulphide, the nickel will be oxidised, and, in the presence of silica, will form a slag. Nickel, therefore, cannot be reduced from its sulphide by the use of a blast, in the same way as copper is separated by "Bessemerizing" copper matte.

The compound present in nickel-matte is always NiS. Nickelous sulphide Ni_2S does not exist. If the sulphur in a sample of nickel-matte is not sufficient for the formation of monosulphide, the excess of nickel will be in the metallic state. Molten nickel sulphide has the power of dissolving metallic nickel, which separates on cooling.

There is no action between nickel sulphide and the oxides when heated together. So it is impossible to extract nickel by a process similar to that for copper.

Further, the sulphide does not react with the oxides of iron.

According to Schweder[1] the sulphide and cupric oxide react as shown by the following equations:—

$$4CuO + 4NiS = 2Cu_2S + (NiS + Ni) + 2NiO + SO_2.$$
$$4CuO + 2NiS = Cu_2S + 2Cu + 2NiO + SO_2.$$
$$4CuO + (2NiS + 2Ni) = Cu_2S + 2CuNi + 2NiO + SO_2.$$

Nickel sulphide at a red heat is slowly and incompletely oxidised by steam.

Carbon and hydrogen decompose the heated sulphide very slowly, forming carbon bisulphide and sulphuretted hydrogen respectively. Carbon monoxide has no appreciable effect.

When the sulphide is melted with an acid iron silicate, a very small quantity of nickel passes into the slag.[2]

If cobalt sulphide is present a considerably greater quantity thereof passes into the slag.

If compounds or mixtures of iron, copper and nickel sulphides are melted with sodium sulphate and carbon, or with sodium sulphide, the iron and copper sulphides make, with the sodium sulphide, a matte in which there is only a small proportion of nickel sulphide; by far the greater portion of this last passes into a nickel matte with only a small quantity of the other two sulphides. The former matte is more easily fusible, and less dense than the nickel matte, and collects above it, so that the two kinds can be easily separated. Repeating the treatment in the same way on this nickel matte, iron and copper can be almost completely removed, and finally nickel sulphide obtained alone.

If any mixture of the three sulphides is roasted with common salt, the copper is converted into chloride, and the iron and nickel are oxidised. This chloride can be removed from the mixture of oxides by lixiviation, cupric chloride by water, cuprous chloride by alkaline chlorides, or weak hydrochloric acid.

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[1] *Berg. und H. Ztg.*, 1878, p 377; 1879, p. 17.

[2] Badoureau, *Ann. des Mines*, 1877, p. 287. *Berg. und H. Ztg.*, 1878, pp. 185, 205, 228, 244—259.

NICKEL AND ARSENIC

Nickel has a great affinity for arsenic, and combines with it in very different proportions. The compounds are known as nickel speiss.

If nickel arsenide is roasted, the arsenic forms arsenious oxide, the nickel sesquioxide. Part of the arsenious oxide escapes unaltered, part is further oxidised to arsenic oxide (As_2O_5) and this combines with nickelous oxide to form an arseniate. Nickel arseniate is not decomposed when heated alone, so the result of the roasting is basic nickel arseniate.

This arseniate is reduced by carbon to a nickel arsenide which contains less arsenic than the one originally roasted. Such a reduction takes place, to a certain extent, during the oxidising roasting, by mixing the charge with powdered coal or carbonaceous substances (sawdust or pine-needles). By repeating the roasting a further proportion of arsenic is expelled, and by melting the product in a reducing flame a nickel arsenide containing less arsenic is again obtained. By a repetition of roasting and smelting under proper conditions it is possible to reduce the arsenic in nickel to a very small proportion. The last portions may be removed by melting the compound with saltpetre and soda. The arsenic is thereby converted into sodium arseniate, which can be separated from the nickel monoxide by lixiviation.

Nickel speiss frequently contains iron, cobalt and copper. When this is roasted, a mixture of oxides, arseniates and undecomposed arsenides of these metals is obtained.

By stirring carbonaceous matter into the charge, iron arseniate is chiefly converted into ferric oxide, while the arsenic oxide is converted into arsenious oxide and arsenic suboxide, with the formation of carbon dioxide.

If sulphides are mixed or combined with these arsenides, sulphates are formed by roasting.

In addition to sulphates so formed, the arsenides themselves may be converted into sulphates by the vapours of sulphuric acid formed in the roasting.

Of the three metals, nickel, cobalt and iron, nickel has the greatest affinity for arsenic, then cobalt, lastly iron.

If a mixture of oxides, arsenides and arseniates of iron and nickel, which contains sufficient arsenic to form Ni_2As with the nickel present, is heated with coal and silica, the whole of the nickel will be converted into arsenide, and the iron into ferrous silicate. More than that proportion of arsenic will cause the formation of a nickel speiss containing iron arsenide.

Similarly if mixtures of oxides, arsenides and arseniates of nickel, cobalt and iron, which contain sufficient arsenic to form Ni_2As and Co_2As, are heated with coal and silica, the nickel and cobalt will form arsenides and the iron will be slagged as ferrous silicate. If less than that amount of arsenic is present, some cobalt passes into the slag and carries with it a minute quantity of nickel, while more than that quantity of arsenic leads to the formation of cobalt-nickel speiss which contains iron arsenide.

Copper, in presence of coal and silica, will, if sufficient arsenic be present, pass into the speiss more readily than iron; if the arsenic is not sufficient for this, the copper is either separated in the metallic state or passes into the slag as cuprous silicate.

If sulphur is present as well as copper in the mixture of oxides, arsenides and arseniates, the copper combines with the sulphur even when there is quite enough arsenic for its arsenide to be formed. If copper and sulphur are in greater proportions the sulphur compound forms a separate matte.

If nickelous and cobaltous oxides and cupric oxide are fused with silica and iron arsenide, containing sufficient arsenic, a nickel-cobalt-copper speiss is produced, while the iron forms a ferrous silicate.

According to Badoureau,[1] when nickelous and cobaltous oxides are fused with arsenic or arsenical pyrites, almost the whole of the nickel and only part of the cobalt pass into the speiss.

If a nickel-iron speiss is fused, and air passed over it, the iron is oxidised first and converted into slag by the addition of silica. The nickel is oxidised only after the removal of the iron. The process can be so conducted that only the iron is removed, the nickel being left as arsenide. If cobalt is present in this speiss, it is oxidised and passes into slag after iron, but before nickel. The appearance of cobalt in the slag is detected by its blue colour. Therefore if it is desired to keep the cobalt in the speiss, the process of oxidation must be stopped as soon as the blue colour appears in the slag. As a certain quantity of nickel goes with the cobalt, the blue coloration shows also the presence of some nickel in the slag.

If heavy spar, instead of quartz, is added during this fusion, the iron may be completely separated, for heavy spar and iron arsenide react, forming iron arseniate and barium sulphide, both of which are taken into the slag. Any copper present is converted into sulphide by the barium sulphide, and separates as a matte if in considerable quantity.

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[1] *Loc. cit.*

NICKEL SULPHATE

Nickel sulphate ($NiSO_4 + 7H_2O$) is soluble in water. At a high temperature it is decomposed into nickel monoxide and sulphur trioxide, or, rather, sulphur dioxide and oxygen. It is more stable when heated than the sulphates of iron and copper. A mixture of all three sulphates can be heated so that the iron and copper compounds are broken up into the oxides, sulphur dioxide and oxygen, while nickel sulphate is almost all undecomposed, and can be separated from the mixed oxides by lixiviation with water, or, if it is the basic sulphate, with dilute acid.

If it is heated to redness with carbon, it is reduced to nickel sulphide, with the formation of carbon dioxide, but a portion of the sulphate is always reduced to metallic nickel, with the formation of carbon dioxide and sulphur dioxide; this nickel is retained in the sulphide.

Carbon monoxide and hydrogen also reduce the sulphate to sulphide at a red heat.

From a solution of nickel sulphate, nickel is precipitated as sulphide by alkaline sulphides; as nickelous hydrate by potash, soda, milk of lime or milk of magnesia; and by sodium carbonate as basic carbonate.

It may be electrolysed, nickel appearing at the cathode, the acid radicle at the anode. The double sulphate with ammonium, $Ni(NH_4)_2(SO_4)_2$, is used for depositing nickel by electrolysis.

CHLORIDE OF NICKEL

Nickelous chloride is soluble in water. Its reactions are similar to those of the sulphate. The solution, when electrolysed, gives nickel at the cathode, chlorine at the anode.

SILICATES OF NICKEL

Nickel silicates, when reduced by carbon, yield metallic nickel, if suitable bases are present to form a slag with the silicic acid. Nickel, like iron, dissolves carbon and silicon, and therefore, if a nickel silicate containing iron is smelted with coal and fluxes, we have, by reduction of some of the iron, an iron-nickel alloy containing both carbon and silicon.

When the silicate is smelted with iron pyrites, with copper pyrites, or with sulphides of the alkalies and alkaline earths, nickel is reduced, and forms a matte or mixture of matte and metal.

If it is smelted with arsenic or arsenical pyrites, it is very incompletely converted into nickel speiss.

The mineral garnierite, a nickel-magnesium silicate, is soluble in sulphuric and hydrochloric acids.

NICKEL CARBONYL, $Ni(CO)_4$

This compound is formed if carbon monoxide is passed over nickel at temperatures between 50° and 150° C. It is a liquid boiling at 43° C., and solidifying at $-25°$ C. At 200° C. it is decomposed into nickel and carbonic oxide. Its vapour is very poisonous.

ALLOYS OF NICKEL

Nickel alloys with many metals, and it is principally used in the form of alloys, especially those with copper and zinc, known by various trade names, such as german silver, argentan, white metal, queen's metal; and the iron-nickel alloys ferro-nickel and nickel-steel. Silvered argentan is known as china-silver, packfong and Christofle's metal.

German silver usually contains 5 parts copper, 2 of nickel and 2 of zinc. Nickel alloys are employed for the subsidiary coinages, known as billon, in several countries; for instance, the coinages of Germany, the United States (since 1866), Belgium (since 1860), Brazil (since 1872), Venezuela (1877), are all 75 per cent. copper, with 25 per cent. nickel. In Chili the composition of the coins used since 1873 is 70 per cent. Cu, 20 per cent. Ni, 10 per cent. Zn.

At the present time a large quantity of nickel is used in producing "ferro-nickel," of which armour-plates, guns and other weapons are manufactured. It was discovered recently at Creusot that from 3 to 27 per cent. of nickel added to iron materially increased its elasticity and tenacity. The ferro-nickel made at the Cockerill Works at Seraing (Belgium), and used for arms and artillery, contains 7·5 per cent. nickel and 0·06 per cent. carbon. The armour plates of the Bethlehem Iron Co. at Chicago contain 3·25 to 3·5 per cent. nickel and 0·35 per cent. carbon. Those of the Wittkowitz Works in Mährisch-Ostrau contain 8 per cent. nickel and 0·2 per cent. carbon.

At Bethlehem they make also nickel-steel containing 27·5 per cent. nickel.

In making ferro-nickel the nickel is added to the charge of iron in the Martin process, and may be used in the form of metallic nickel or monoxide. When small quantities of the oxide are used it is reduced by the carbon in the iron, but if large quantities are used, coal must be added for reduction.

It appears that the Carnegie Co. at Homestead[1] have bought a patent of their engineer's, according to which nickel monoxide, with more or less iron, is made into bricks with coal, or organic agglomerants, and charged into a Martin furnace.

By Harvey's method, used in the United States, plates of nickel-iron are converted by cementing into steel plates on one side only, after which they correspond in hardness and temper to iron and steel compound plates. The plates treated in this way resemble iron on one side, and steel on the other, and for this reason prove to be valuable.

At present nickel-steel is the best material for armour plates, turrets and shields.

The present high price of nickel-iron alloys, and certain technical difficulties in their production, prevent their extended use in construction.

Nickel, when alloyed with metals more oxidisable than itself (*e.g.*; copper), can be separated by an oxidising fusion.

ORES OF NICKEL

Nickel occurs only in combination. In compounds it may be the chief element, or in small proportion to the other metals present.

In the extraction of the metal, not only nickel ores proper are important, but also those minerals which contain nickel in small proportion as a secondary element, or contain it, combined with other elements, as an impurity.

The greatest quantity of nickel is obtained at present from the silicate *garnierite*, or from magnetic pyrites containing nickel.

We may quote the following as true nickel ores :—

Kupfernickel or *arsenical nickel*, NiAs, containing 43·5 per cent. Ni. The nickel in this ore is often replaced by cobalt and iron in small proportion; the arsenic may be replaced by antimony up to 28 per cent., and in small proportion by sulphur. It has been found, or is

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[1] V. Ehrenwerth, *Das. Berg- und Hütten-wesen auf der Weltausstellung in Chicago.* Vienna, 1895.

still got, in Germany (Riechelsdorf, Olpe, Sangerhausen, Kamsdorf, Schneeberg, Annaberg, Harzgerode, Wittichen); in Austria (Schladming, Leogang, Dobschau): in France (Allemont in Dauphiné, Balen in Basses-Pyrenees); in England (Pengelly, Fowey, St. Austell in Cornwall); and in Scotland (Bathgate).

White nickel-ore, or *chloanthite*, $NiAs_2$, is composed of 28·2 per cent. nickel and 71·8 per cent. arsenic. Frequently a small proportion of the nickel is replaced by cobalt and iron. This mineral is found in the same places as the other arsenide.

Breithauptite or nickel antimonide (NiSb), with 31·5 per cent. Ni, (St. Andreasberg in the Harz); *ullmannite* or *nickel antimony glance* ($NiSb_2+NiAs_2$) with 26·1 per cent. Ni (at Siegen); *gersdorffite nickel glance*, or *nickel arsenic glance* ($NiAs_2+NiS_2$), with an average percentage of 35 Ni (Siegen, Schladming, Harzgerode, Helsingland); *annabergite*, *nickel ochre* or *nickel bloom* ($Ni_3As_2O_8+8H_2O$) with 29·5 per cent. Ni (occurring in the upper seams of nickel-ore deposits); *moresonite* or *nickel vitriol* ($NiSO_4+7H_2O$) (occurring similarly). All these ores occur in such small quantities that they can never be singly worked for nickel.

Millerite, or *hair pyrites*, *nickel pyrites*, NiS, with 64·5 per cent. Ni is occasionally found pure in large, independent masses, more often combined intimately with iron and copper pyrites. (At Nanzenbach near Dillenburg, Gapmine in Pennsylvania, Sudbury in Canada, Arkansas.) This mixture of all three pyrites forms a valuable source of metallic nickel.

Iron and nickel pyrites, or *necopyrites* (2FeS + NiS) with 18 to 21 per cent. Ni, is found at Lillehammer in Southern Norway.

Garnierite is a nickel magnesium silicate, containing water of crystallisation, discovered in 1863 by Garnier in the island of New Caledonia. It fills up clefts and fissures in a serpentine, formed by the metamorphosis of enstatite, a magnesium silicate, and is accompanied by several such silicates, by *chrysoprase*, *magnetite*, *chromite*, and other minerals. Its extensive occurrence in this locality has caused it to become the chief source of metallic nickel, after the nickel-holding pyrites (magnetic and copper) of Sudbury in Ontario. The usual composition of *garnierite* is—

9—17	per cent.	NiO.
41—46	„	SiO_2.
5—14	„	Fe_2O_3.
1— 7	„	Al_2O_3.
6— 9	„	MgO.
8—16	„	H_2O.

Very occasionally it contains as much as 40 per cent. Ni. The average percentage of nickel in the ores of late years has been 7 to 8. The quantity of iron contained, which is only mechanically mingled, often exceeds the nickel. The composition of garnierite varies according to the particular magnesium silicate which forms its basis. By the analyses of Garnier and Thiollier the composition $(NiMg)SiO_3 + nH_2O$ has been assigned to it.

A nickel-magnesium silicate similar to this, containing 8·96 per cent. Ni in the impure condition, was discovered by Meissonier in 1876 in the province of Malaga in Spain. Its occurrence is slight. Very recently, also, near Riddle Station in Oregon, a nickel-magnesium silicate has been found with an average of 5 per cent. of nickel.

Amongst nickel compounds of similar composition we have also *rewdanskite* at Rewdansk near Ekaterinenburg in Ural, *genthite*, occurring in Texas and Pennsylvania, and *pimelite* at Reichenstein in Silesia. These minerals are all found in such small quantities that they cannot form the foundation for a special extraction of nickel.

Among ores in which nickel is not the chief element we note especially certain pyrites, the chief being magnetic and copper pyrites. Many varieties of arsenical pyrites also contain nickel.

Iron and copper pyrites, as above, are found in the neighbourhoods of Nanzenbach (before mentioned), Gladenbach, and St. Blasien in the Black Forest. The Nanzenbach ore has an average of 5 per cent. Ni and 5 per cent. Cu; St. Blasien ore 2 to 2·5 per cent. Ni and 0·75 per cent. Cu. Magnetic pyrites containing nickel is found in Sweden (Klefva and Smaland, Hudigswall, the neighbourhoods of Gefle, of Fahlun, and of Sagmyrna); in Norway (Langesund Fiord, Ringerick nickel-mine near Nakkerud, Krageröe, Moss, Snarum, Christiansand); in Piedmont (Varallo), Pennsylvania (Lancaster Gap Mine), Massachusetts (Dracut), Oregon, and largely developed in Sudbury (Canada). The proportion of nickel is, at Klefva 1·5 per cent., at Sagmyrna 0·5 to 0·8 per cent., Krageröe 1·75 per cent., Varallo 1·20 to 1·44 per cent., Gap Mine in Pennsylvania 1·75 per cent. (with 1 per cent. Cu and 0·1 per cent. Co). The copper pyrites at the Ringerick Mine in Norway contain 33·24 per cent. Cu, 0·42 to 1·75 per cent. Ni, and 0·01 per cent. Co. The magnetic pyrites (*pyrrhotite*) at Sudbury is found in large lenticular accretions in diorite dykes in the Laurentian and Huronian formations; it contains 1·5 to 9 per cent. Ni and is mixed with copper pyrites. The average amount of nickel is 3 per cent. and something over 3 per cent. is copper. As the depth of the vein increases the percentage of nickel seems to increase, that of copper to decrease. For example, in the upper levels of the Copper Cliff Mine the quantity of copper is 4 per cent., of nickel 4·5 per cent.; while at the deepest present level the quantity of copper has sunk to 0·5 per cent., and that of nickel has risen to 8 or 10 per cent.

The Sudbury ore is at the present time the principal source of nickel.

The arsenical pyrites containing nickel at Dobschau in Hungary contains from 0·25 to 17 per cent. Ni; the same sort of ore at Schladming in Styria contains 11 per cent. Ni and 1 per cent. Cu.

METALLURGICAL PRODUCTS USED AS A SOURCE OF THE METAL

When ores of lead, copper, cobalt or silver are smelted, any nickel which they contain collects in the speiss. Should the ore be free from arsenic, so that a speiss is not formed, the nickel will be found in the various intermediate products—matte, blister-copper, tough pitch copper and lyes; or in final products like slag or scars; from all of these it can be extracted.

THE EXTRACTION OF NICKEL

This may be done:—

I. By the dry method.
II. By the wet method.
III. Electro-metallurgically.

The dry method should be used for ores and metallurgical products containing a large or a medium quantity of nickel, if it is possible to get a pure metal (or oxide) out of such ores, without the help of a wet method. It is also satisfactory when the purity of the product is not essential.

With poor ores the dry method can be used, if the nickel can be concentrated without great cost in an intermediate product (a matte or speiss), and if from this latter nickel or nickel oxide can be got pure without recourse to a wet method, or, again, if a pure metal is not the object.

Wet methods are used for ores which are poor in nickel, and for which concentration of the nickel in a matte or speiss would be too expensive.

Wet methods are also used for intermediate products, when it is desired to produce from sources of nickel in which copper is an impurity, a nickel oxide or metallic nickel which shall be free from copper; they are also employed when the desired products are more profitably obtained by these methods: such are the metal, alloys or salts.

Electrolytic methods have not been applied to ores so far, nor have they been much used for intermediate products. In view of the difficulty of obtaining compact nickel by means of an electric current, it is doubtful whether these methods will ever be greatly used.

Metallic nickel may contain many impurities, such as the oxide, and mechanically enclosed gases, which would restrict its application in the arts. In such cases a purification by some special refining process is necessary, and dry methods are generally used for this purpose. Most nickel smelters are in the habit of producing only a speiss or matte, which is further treated for the extraction and purification of the nickel by the manufacturers who keep their processes secret.

Nickel monoxide has been manufactured in large quantities for the production of ferro-nickel: it is added, either alone or with a reducing agent, to charges of iron or steel. If it is used in small quantities with cast iron, there is usually sufficient carbon present in the latter to act as a reducing agent. Nickel oxide is also used in the manufacture of pigments.

I. Extraction of Nickel in the Dry Way

A. EXTRACTION FROM ORES

The most important ores at present are the sulphur compounds and the silicates, the arsenic compounds taking the second place. Apart from the Mond process, which consists of preparing nickel carbonyl, and decomposing this into nickel and carbon monoxide,—a process which has not yet been successful on a large scale—the ores mentioned must be utilised in different ways. Therefore the extraction of the metal from each class of ore is best considered independently.

I. EXTRACTION OF NICKEL FROM SULPHUR COMPOUNDS

The compounds to be considered are magnetic and other pyrites containing nickel, frequently mixed with copper pyrites. They may be classified generally as compounds in which sulphur and iron are the chief elements, with, in addition, a small proportion of nickel and copper. The proportion of nickel varies between 1 per cent.

and 5 per cent. Pure nickel sulphide, hair pyrites or millerite, does not occur in such quantities that it can be treated alone for nickel, but it occurs often in the above ores, and so finds its way into the smelting processes.

In smelting these ores in the dry way, after getting rid of gangue, we are chiefly concerned with the separation of the nickel from sulphur and from iron, and in most cases also from copper. If no copper is present, the process becomes so much the simpler.

With ores free from copper the extraction depends principally on the fact that iron has a greater affinity for oxygen than either nickel or sulphur has. Thus it is possible to remove iron from these ores as oxide, and slag it, the nickel being separated chiefly as sulphide. Then at a higher temperature atmospheric oxygen will convert this sulphide into monoxide, which must be reduced by carbon.

The formation of the sulphide is effected by roasting and smelting operations, the conversion to oxide by roasting, and reduction of the oxide by ignition with a reducing agent or smelting.

Owing to the small proportion of nickel in most ores (1 to 5 per cent.), it is not possible to obtain the sulphide from them by a single smelting and roasting. It is most usual to adopt a procedure similar to that employed for the separation of copper from sulphide ores containing iron, and thus to produce, by roasting and subsequent reduction, a nickel-iron matte. This matte, containing iron but with an increased proportion of nickel, is converted by fusion in an oxidising atmosphere into a matte free from iron. But if this first matte is still poor in nickel, further concentration by the same methods takes place before this final fusion.

The matte obtained free from iron is subjected to dead roasting, often in two operations, and becomes nickelous oxide, which, as already said, is reduced to nickel by fusion with a reducing agent.

The first operation to which the ores are subjected, the roasting, converts all the metallic sulphides into a mixture of oxides, sulphates and undecomposed sulphides.

In the next process, the smelting of the roasted product in a shaft-furnace with coal and siliceous matter, nearly all the iron passes into the slag, while any small proportion of iron sulphide still remaining undecomposed by both processes, forms a matte containing all the nickel sulphide.

It is necessary to retain considerably more sulphur than is required to combine with nickel in the roasted product, because none of the small proportional amount of nickel present can be allowed to pass into the slag. Consequently the matte will contain a large quantity of iron sulphide. From this matte, known as raw nickel matte, the iron is separated, with the corresponding amount of sulphur, by an oxidising fusion in hearths, reverberatory furnaces or converters. If it is poor in nickel and rich in iron, it is better first to concentrate the nickel by another roasting followed by a reduction with coal and silica as above, in a shaft furnace, or in a reverberatory furnace without reducing agent. The chemical changes with nickel coarse matte are just the same as with the ore direct, except that there is no longer any gangue to form slag.

When the roasted ore is smelted in a reverberatory furnace the ferric oxide present is reduced by the sulphur of the iron sulphide to ferrous oxide, in the presence of the silica, and sulphur dioxide passes off. The equation is as follows:—

$$FeS + 3Fe_2O_3 + xSiO_2 = 7FeOxSiO_2 + SO_2.$$

Meanwhile the nickel monoxide present reacts with an equivalent quantity of ferrous sulphide to form nickel sulphide and ferrous oxide, which last forms slag. The result, then, of this smelting in a reverberatory furnace is nickel sulphide with a greater or less quantity of iron sulphide, according to the amount in the raw matte, and ferrous silicate.

If the matte or the concentrated matte, in the unroasted condition, is subjected to an oxidising fusion in a reverberatory furnace with silica, the iron will pass into the slag as ferrous oxide, while nickel sulphide is unchanged. Some nickel oxide reacts with ferrous sulphide, and, as before, the results are nickel sulphide with more or less iron sulphide, and ferrous silicate.

In this process also an admixture of heavy spar and coal, or of Glauber salt and coal, works satisfactorily, as the coal causes barium or sodium sulphide to be formed, and this converts oxidised nickel back to sulphide, and the baryta or soda formed makes a very fusible slag with silica.

If the raw nickel matte or a concentrated matte is subjected to an oxidising fusion on a hearth under a stream of compressed air, the iron is oxidised to ferrous oxide and forms a slag with the silica of the furnace lining, while nickel sulphide is unchanged. If the oxidation is carried on sufficiently long, there will be only traces of iron sulphide left behind. But a considerable loss of nickel in the slag occurs if the iron is completely separated.

The separation of iron from nickel matte by means of the Bessemer converter is rapid and complete. Besides the iron any arsenic and antimony present in the matte are completely removed. The iron is converted into ferrous oxide by the stream of air blown into the molten matte, and forms a slag with the silica of the converter lining, or else with quartz added. Any nickel which may be oxidised reacts with whatever ferrous sulphide may be left, thus giving ferrous oxide which is slagged, and nickel sulphide. The process finally gives this sulphide and a ferrous silicate which will always contain a certain quantity of nickel.

It is not possible to separate the nickel as metal in the converter by continuing the blast, as is done in separating copper from its sulphide in the copper-Bessemer process. In addition to the fact that nickel oxide and sulphide will not react, it is not possible at the temperature required in the process to oxidise the sulphur without oxidising the nickel as well. Indeed with a certain proportion of nickel and sulphur in the matte, nickel is more easily oxidised than sulphur. Finally, the heat developed in the oxidation of nickel sulphide is not enough to fuse nickel.

When the nickel ore contains copper, as is generally the case, the copper remains in the matte owing to its great affinity for sulphur, and thus the oxidation followed by reduction gives a matte containing sulphides of nickel, iron and copper. Iron can be separated from this in exactly the same way as when copper is not present, and we obtain a matte consisting of nickel and copper sulphides. This is usually worked up into nickel-copper alloys. For this purpose the mixed metals are oxidised by roasting and the alloy obtained by smelting with coal.

If the ore or matte has only a small proportion of copper, it can be treated exactly as if free from it; and then there results a nickel containing copper, which is of special use in making alloys. But if nickel or the oxide quite free from copper is required, as, for instance, for ferro-nickel, the copper must be separated by some special process, either from the first matte after smelting the ore or from a concentrated matte, or from the nickel-copper alloy. These special processes to separate copper may be wet or dry.

The dry method has generally been to smelt the matte with Glauber salt and coal; the copper then forms with the iron present a compound sulphide of sodium, copper and iron, and nickel sulphide remains behind. Or the copper is converted into chloride by chlorinating and lixiviating the matte. A wet way which has lately come into use is to dead roast the matte and dissolve all three oxides in acids. Then copper, iron and nickel are separately precipitated. It appears that electrolysis has also been used, but details have not been published.

According to the above explanation we must distinguish the following processes in the working up of sulphuretted ores of nickel into crude metal or into copper-nickel alloys.

a. Conversion of the ore into a coarse matte.

b. Separation of iron from the latter, or "refining."

c_1. Working up of refined nickel-copper matte into copper-nickel alloys.

c_2. Working up of the same nickel-copper matte into a matte free from copper.

d. Working up of the products from 2 or 4 into nickel oxide or crude nickel.

a. THE CONVERSION OF THE ORE INTO COARSE MATTE

This process consists in roasting, followed by the reduction of the roasted product in shaft furnaces. In exceptional cases, when the ore is mixed with large quantities of earthy gangue, the roasting is dispensed with, and the unroasted ore smelted to get rid of the gangue as slag.

a. ROASTING THE ORE

The ore to be roasted is magnetic pyrites and iron pyrites, mixed with copper pyrites, and often with arsenic and antimony compounds, and also with silicates, quartz and earthy matter.

During roasting the aim is to get rid of sulphur until enough only remains to combine with nickel, copper and a portion of iron, during the smelting to follow. If cobalt is present it will be wholly combined with sulphur. Arsenic and antimony are removed as completely as possible.

We have seen already that as the proportion of nickel in the ore is so slight (1 to 4 per cent., rarely above 5 per cent.), it is impossible to decompose all the iron sulphide in roasting, for then in smelting, nickel would pass into the slag with the iron; and further, as it is impossible in these circumstances to avoid the formation of iron sows, the nickel will be reduced and pass into them. It must depend on the relative proportions of nickel, cobalt, iron and sulphur in the ore, how much sulphur can be oxidised away. When possible, ores containing 4 to 5 per cent. nickel, or more, should be so worked that smelting gives a matte with 15 or 20 per cent. nickel without any serious loss of the metal. Poor ores with 1 or 2 per cent., should give a matte with 5 to 10 per cent.; for here loss of nickel in slag and sows has a greater proportional effect than with richer ores. If there is any cobalt in the ore, the roasting must be stopped so much the sooner. When the cobalt is worth separating there must be an excess of sulphur in the roasted product, for cobalt has less affinity for sulphur than nickel has, and so will pass into the slag before the latter does.

In the roasting the sulphur partly escapes as dioxide, and is partly converted into trioxide by contact with red-hot masses of ore and red-hot furnace walls. Iron, copper and nickel oxides combine with this trioxide to form the three sulphates. As the roasting proceeds and the temperature is raised, the sulphates are again decomposed into oxides and sulphur trioxide, or sulphur dioxide and oxygen. Iron sulphate is first decomposed, next the copper, lastly the nickel compound.

If the roasting were kept up long enough at the proper temperature, the product would be a mixture of ferric oxide, nickelous oxide and cupric oxide. But if it is stopped after a certain quantity of sulphur in the ore has been got rid of, as is nearly always necessary, in order to produce the matte, the product will be a mixture of oxides, sulphates and undecomposed sulphides. Ferric oxide, ferric sulphide and basic ferric salts preponderate in quantity. If zinc blende was present in the ore, zinc sulphide and oxide and neutral and basic sulphate are found in the product. If arsenic and antimony were present, arseniates and antimoniates are found as well as undecomposed arsenides and antimonides. We should find lead sulphide, oxide and sulphate resulting from galena in the ore. Quartz, heavy spar and silicates remain unaltered. Calcium carbonate will become sulphate.

The Operation of Roasting.—This may be carried on in heaps, kilns, shaft-furnaces reverberatory furnaces, or muffles. The choice among these methods depends on the necessity for disposing of noxious gaseous products, on the possibility of using these products in the manufacture of sulphuric acid, and on the cost of fuel and labour.

The roasting of lump ore in heaps takes a long time, is imperfect in its results for many ores, and provides no way of disposing of or utilising the gases set free; further, it causes loss of metal by the washing away of nickel and copper sulphates, unless it is carried on under cover; on the other hand, it means only slight cost of plant, a small amount of labour, and a small consumption of fuel, especially if the ore is rich in sulphur.

The fine roasted ore ("smalls"), if it is not moulded into lumps, serves as coverings and bottoms for the heaps of lump ore. The moulding entails a good deal of labour, while roasting up to the required limit requires a definite proportion of fine among the lump ore. Otherwise the roasting of fine ore in heaps has the same disadvantages as roasting lump ore.

This method is used when the utilisation of the gaseous products, for sulphuric acid or otherwise, is not feasible, on account of there being no market for the product, or because the nature of the ore is not suitable; and when, at the same time, the situation and neighbourhood are of so little value that they are not seriously deteriorated by the noxious gases escaping; it may also be used where fuel and labour are dear. These conditions are met with in the chief place for roasting sulphuretted nickel ores, the neighbourhood of Sudbury in Ontario, and also to some extent in Sweden and Norway.

The Canadian ores are magnetic pyrites containing about 3 per cent. nickel and 3 to 4 per cent. copper. There is no sulphuric acid plant at Sudbury. The great compactness of the ore and its small proportion of sulphur are against its being roasted profitably in shaft furnaces, kilns, pyrites burners or Maletra furnaces, such as are used in the sulphuric acid manufacture. To get gaseous products suitable for such manufacture, these ores must be mixed with others, or roasted in muffles. Further, it is not worth while to export an ore so poor in nickel to a place where its sulphur could be utilised. The best economy at present is to convert the ore into a nickel matte on the spot without concern for either utilising or rendering harmless the gaseous products. So the roasting of the ore is carried out simply in heaps. We find similar conditions in Sweden at Klefva and Sagmyrna, and in Norway at the Ringerick nickel factory, and at Kragerö, in which places the nickel works are mostly at present out of work. The ore is poor, there is no market for sulphuric acid, and land is not dear. So here roasting in heaps is convenient.

Roasting in stalls entails a great expenditure of time, like roasting in heaps; it means also a greater initial outlay and more labour, and it endangers the health of the labourer during the emptying of the stalls. It precludes the utilisation of the oxidised gases, but steps are taken to diminish the noxiousness, by leading them into high chimneys. By careful management of the draught, the method will yield a more even roasting, and in a shorter time, than roasting in heaps. The quantity of fuel used is as low for ores rich in sulphur as in heap-roasting; finely divided ore can only be used as bottoms and coverings unless it is consolidated.

Stall roasting is therefore used where the sulphurous gases cannot be utilised, but where their injurious effects are bound to be limited as far as possible by leading them into high stacks.

Formerly these stalls were used at Dillenburg (the Isabella Works) and at the Sesia Works at Varallo, in Piedmont.

Shaft furnaces are used for ores rich in sulphur, both lump and fine, if the gases are to be used for sulphuric acid. This use of the gases presupposes such a proportion of sulphur and composition of ore that the roasting temperature can be kept up by the heat evolved in the oxidation of the sulphur, and that the ore is thoroughly burned through without leaving cores. The ore must not melt, nor even sinter, and the lumps of ore must not decrepitate at the temperature.

Shaft furnaces may also be used without any concern for the utilisation or rendering harmless of the furnace gases, if fuel is dear and labour cheap, (the gases may be sent straight into the air or partly rendered less noxious by being led into high chimneys,) or may be used when the ore must be rapidly roasted. In such cases lump ore may be also roasted in kilns; pulverulent ore in furnaces of the Gerstenhöfer or Maletra pattern. In kilns, ores poor in sulphur are arranged in layers alternately with fuel.

Any instance of the use of shaft furnaces for the purpose of utilising the gases from nickel ores in sulphuric acid manufacture is not known to the author.

Shaft furnaces have been used at Dillenburg to roast ores of nickel. As the ore (pyrites containing nickel) was mixed with much gangue, the temperature had to be kept up by alternating with layers of fuel.

Roasting in reverberatory furnaces will not allow of the utilisation of the gases; it entails preliminary pulverisation of the ore, and a great consumption of fuel and labour, but it can be performed quickly and can be accurately adjusted to the right stage in getting rid of sulphur. Nevertheless, the costliness of this method has prevented its being used up till now for these sulphuretted ores containing so small a proportion of nickel. It becomes feasible with ores containing much nickel, and when a quick process is necessary, if utilisation of the gases is not desired, or is not suitable to the nature of the ore, in which cases as high a chimney as possible is used.

The use of muffles entails a large expenditure on fuel and labour, but it allows of the using, or rendering harmless, of the gaseous products, and is convenient for stopping the roasting at the proper stage. With the muffles, as with the reverberatory furnaces, the ore must first be reduced to small size. Up till now they have not been used for these sulphuretted nickel ores, because of the expense of the roasting. They may come into use when it is desired to utilise certain ores in sulphuric acid manufacture, which ores are not suitable for roasting in shaft furnaces, either because of their small proportion of sulphur, or because of their sintering, melting or decrepitating.

Roasting in Heaps

This is carried on in the same way as the normal roasting of magnetic pyrites, or of pyrites containing copper.[1]

At Sudbury, in Canada, the ores, magnetic pyrites with about 3 per cent. nickel and rather over 3 per cent. copper, are broken and classified into the three sizes, 4 inches, 1¾ inch, and ¾ inch, and then piled on a bed of wood in heaps of 5 to 15 feet high, 82 feet long, and about 39 feet broad. A heap contains from 600 tons to 3,000 or more. In the middle there is a small chimney to create a draught and carry off the combustion products. To every 20 tons of ore a cord of wood (128 cubic feet) is allowed. The bed is laid upon a layer of fine ore 6 to 10 inches thick, which itself becomes roasted down to a certain depth, generally about half-way. On the bed the coarsest pieces are laid, then the medium-sized, and lastly, fine ore again. The whole heap is covered with a layer of fine ore 6 to 8 inches thick. The length of time for the roasting varies according to the size of the heaps from 6 to 20 weeks. A heap containing 1,000 tons takes 60 to 80 days. By one roasting the proportion of sulphur in the ore is reduced from 30 or 40 per cent. to between 4 and 7 per cent.[2]

At the works at Klefva in Smaland (Sweden), closed at present (1896), the nickeliferous magnetic pyrites was subjected to a single roasting in heaps on a bed of wood, each heap containing 210 tons.[3] This pyrites contains from 1·08 to 2·03 per cent. nickel, and from 0·38 to 1·03 per cent. copper. At Sagmyrna (also closed) the pyrites, containing 0·6 per cent. nickel and 0·7 per cent. copper was roasted three times. Each heap held 300 or 400 tons of ore, and burned 3 or 4 weeks.

At the Ringerick works in Norway (also closed) magnetic pyrites with from 0·42 to 1·75 per cent. nickel was roasted with wood in heaps of about the same size as those at Sagmyrna; they burned for from 1 to 3 months. After roasting, the ore was sorted, and that which was imperfectly roasted put into another heap with fresh ore.

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[1] Vol. i. p. 28.

[2] *The Mineral Industry*, 1894, p. 459.

[3] 5,000 Swedish centners, each 94½ lbs.

Roasting in Stalls

This form of roasting used to be carried on at the Isabella Works at Dillenburg, and the Sesia Works at Varallo in Piedmont. At the former place stalls have been replaced by shaft furnaces.

At the Sesia Works,[1] the pyrites contained from 1·20 to 1·44 per cent. of nickel. It was roasted in stalls about 13 feet long, 10 feet broad, and 10 feet high, with two fires. The charge in a stall was 60 to 80 tons. Two tons of wood were required to roast it.

[illegible] in Shaft Furnaces

At the Isabella [illegible] which have been closed for a long time, the pyrites (averaging 3 [illegible] cent. of nickel, 5 per cent. of copper) was roasted in kilns about 6 [illegible] 6 inches high, 4 feet 6 inches square in section at the upper end, and 2 feet 3 inches square at the lower end. The pyrites is laid in layers alternately with lignite to assist the combustion. The gaseous products were conducted into a chimney 40 feet high, and from 2 to 3 tons of ore were roasted in 24 hours.

At the Gap Mine in Pennsylvania (now worked out), the magnetic pyrites with 1·75 per cent. Ni, 0·1 per cent. Co, 1 per cent. Cu, was roasted in kilns.[2]

β. SMELTING OF THE ROASTED ORE TO PRODUCE COARSE NICKEL MATTE

Matte can be produced directly without roasting when ores poor in sulphur are used. This was formerly done at Kragerö in Norway, where the pyrites containing 1·25 per cent. of nickel was disseminated in a finely-divided state in the rock. Generally, the ores must first be roasted. They then contain a mixture of oxides, sulphates and undecomposed sulphides of nickel, copper and iron, and the greater part of the nickel and of the copper is combined with sulphur. As a rule, metallic arsenides and antimonides, arseniates and antimoniates, quartz, silicates and gypsum are found here. Frequently there are small quantities of cobalt as sulphide, oxide and sulphate.

In the smelting of this ore with coal and fluxes, iron should be slagged as far as possible, and nickel, cobalt and copper collected into a matte. The iron passes into the slag through the reduction of ferric oxide to ferrous, and the combination of this with silica; and also by the decomposition of iron sulphide by nickel oxide, in the presence of silica and coal. This is also brought about by copper oxide when present. Thus the nickel and copper oxides become sulphides, a corresponding amount of iron becomes silicate. Also nickel silicate, generally formed to a certain extent, undergoes a double decomposition with iron sulphide. Copper silicate will behave in the same way. Cobalt silicate is not decomposed by iron sulphide to form cobalt sulphide. Part of the oxides of nickel and copper becomes reduced to metal by carbon monoxide and carbon. Metallic nickel dissolves in the sulphide of nickel present; copper combines with sulphur taken from iron sulphide. Iron will then be separated as metal, unless the iron sulphide is reduced to the combination Fe_2S, a compound not yet isolated. Until the existence of this compound is proved it is better to assume that iron is reduced to metal. This will dissolve in the ordinary monosulphide as nickel does in its sulphide. Further, any ferric oxide present may be reduced by the metal to ferrous oxide and so pass into slag. Another portion of copper oxide reacts with sulphide, as in the English copper smelting process. The copper thus set free will take sulphur from iron sulphide, just as above. Nickel sulphate will be reduced to sulphide, unless the heat decomposes it into nickel monoxide, sulphur dioxide and oxygen. The same applies to copper sulphate. Part of the iron sulphate is decomposed into ferric oxide, sulphur dioxide and oxygen; carbon monoxide converts the rest of it into ferrous oxide and sulphur dioxide, carbon dioxide being meanwhile formed.

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[1] *Berg.-und Hütten. Zeitung*, 1878, p. 185.

[2] *Berg.-und Hütten. Zeitung*, 1874, p. 142; 1875, p. 58.

All these sulphides of nickel, copper, iron, and occasionally cobalt, whether newly-formed by the decomposition of sulphates, or originally present in the roasted ore, unite to form a matte. So long as a considerable amount of iron sulphide is present, there can be but a small quantity of nickel as silicate in the slag, for the double decomposition mentioned above takes place almost completely. The same will apply to copper, but cobalt silicate will remain in the slag.

Antimoniates and arseniates are reduced to metal, and partly volatilise as such. In the presence of undecomposed pyrites part of the arsenic is volatilised as sulphide. The remaining arsenic and antimony, if they are only in small quantities, pass into the matte; otherwise they form a speiss, combined chiefly with nickel and cobalt. Any gypsum will be reduced to sulphide of calcium, which acts with nickel and copper oxides like iron sulphide does.

The quartz and silicates pass into slag. In case the oxide of iron in the charge is not enough to slag it completely, basic slags from a subsequent process or basic ores are added, while if the base prepon-

[illegible]s in the charge quartz and argillaceous ores are added, or acid [illegible] If the ores have been roasted too strongly, so that it is to be [illegible] there will be nickel in the slag, they are mixed with unroasted [illegible] and ores which have been insufficiently roasted, and which [illegible] in consequence yield a large quantity of matte poor in nickel, [illegible] mixed with slags which contain nickel.

Whenever possible the mixing is arranged so as to give a matte with 15 to 25 per cent, nickel. But with the usual ores, poor in nickel, a matte with a lower percentage must be aimed at.

The slag may contain neither too much nor too little silica.

Excess makes the slag less fusible, and in its pasty condition small portions of matte are mechanically enclosed in it; also it requires a great expenditure of fuel, and the raised temperature causes the reduction of iron in the charge. In the same way as iron is reduced in the blast furnace from oxides and even from silicates, so in this charge, which is difficultly fusible owing to its great proportion of silica, iron will be separated as metal, and with it a portion of nickel. This metal sticks fast to the walls of the shaft furnace as the so-called "sows," and the accumulation of these constricts the furnace. In practice the slag is never allowed to contain above 42 per cent. of silica.

Too little silica, which is the same as too much iron, in the slag, makes its density greater, so that it is difficult to separate it from the matte, portions of which are mechanically enclosed. If the furnace is of masonry the brickwork is acted upon, and the slag, from its basic nature, is able to take up the silica and acid silicates. But further, iron is readily reduced from this slag so rich in iron, and again sows are formed in the furnace, and shorten the duration of a campaign. Although too small a proportion of silica is not so injurious as too much, in practice it is advisable not to let it sink below 24 per cent., the lowest limit being 18 per cent.

As determined by practice, the most judicious percentage of silica is between 24 and 36 per cent.

As to the kind of silicates present in the slag, they are between mono- and bi-silicates, the chief base being ferrous oxide. In some cases there may be only mono-silicate, or a mixture of sub- and mono-silicates. Lime, magnesia and alumina may be present as bases to a certain extent, besides ferrous oxide. A relatively small quantity of magnesia and alumina will make the slag refractory, while lime may be present in larger quantity.

The smelting of the ore takes place in shaft furnaces. Very recently these have been constructed like the new shaft furnaces for smelting roasted copper ores containing iron,[1] with circular, elliptical or rectangular horizontal section. By their use the same advantages are obtained as when they are used for copper ores, namely greater output and a greater economy of fuel. Furnaces of this sort are, therefore used largely for smelting roasted nickel ores containing sulphur. At the Canadian Copper Co.'s works in Sudbury a Herreshof furnace is used with a water jacket, 8 feet 10 inches high, 6 feet 3 inches in the longer side, and 3 feet 3 inches in the shorter side of a section of the furnace at the level of the tuyeres. In this furnace 125 tons of ore are smelted in 24 hours.

The height of the furnace depends on the amount of iron in the charge, and the kind of fuel. The higher it is the easier will reduction of iron take place. The greater the amount of iron therefore the lower the furnace. When wood charcoal is used the furnaces are built higher than with coke under similar circumstances; for the combustion of wood charcoal draws quickly upward, and thus with a low furnace part would be burned uselessly at the top.

Usually the height varies from 6½ to 20 feet. With coke it seldom goes beyond 14½ feet, from bottom to throat; with wood charcoal it may be 20 feet. The height from the tuyeres up to the throat is from 6½ to 10 feet with coke, from 13 to 16½ feet with wood charcoal. In the Herreshof furnace at Sudbury, with water jacket and elliptical cross section, and burning coke, the height from the tuyere level to the throat is 6½ to 10 feet.

The cross section should be circular, rectangular, or oval. The pressure of the draught varies between ½ inch and 2 inches of mercury, except in extraordinary cases. The diameter of the furnace, or the shorter side of the rectangle, at the level of the tuyeres, is from 2 feet 6 inches to 4 feet 4 inches, and a little greater at the throat. It varies according as the ore is more or less fusible, and as the pressure must be low or high. (For the structure and dimensions of the furnace see under copper smelting.[2])

The tuyeres are distributed as symmetrically as possible round the circumference of the tuyere level. In old furnaces the tuyeres were in the back wall of the furnace. The blast is supplied usually by a Root's blower, and is not heated for fear of promoting reduction of the iron.

The arrangement of the furnace, when there is much iron present, is best as *spurofen*, for if the molten mass remains too long in the furnace, there will be a separation of iron, and sows may form on the furnace walls. The receivers (*spurtiegel*) to collect the matte are lined with brick, or brasque of clay and coal-dust. Iron cannot be used, as it is readily acted on by the matte.

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[1] Vol. i. p. 90.

[2] *Ibid.*

In Sweden (Klefva, Sagmyrna) furnaces have also been used built on the *sumpf-ofen* pattern.

The construction of the water-jacket furnace used at Sudbury is shown in Figs. 318, 319.[1]

X is the water jacket made of steel plate. The water space, *w*, within it is about 2 inches wide. *U* is the blast-pipe. The furnace is built with an independent forehearth (*spurofen*). The molten mass flows out of it through the water-jacketted pipe *i*, made of bronze, into the collecting cistern *T* carried on wheels. The collecting cistern is surrounded by a water-jacket at the sides, has a movable lid, and a fire-clay bottom. The slag runs out at the upper exit *S* (slag-notch), while the matte is tapped through the tap-hole *t*, provided also with a double-walled, cooled, bronze pipe. The bottom of the furnace is formed of a circular plate, on top of which is a thin layer of sand, and then a course of fire-brick. Above this a portion of the fused charge, reaching to the lower level of the tap-hole, is allowed to solidify, and over this latter the fused mass flows through the tap-hole into the receiver. During the working the molten mass is continuously above the tap-hole, so that the blast cannot blow out there. During the tapping the slag hole is stopped by clay, so here also the blast cannot escape. In other furnaces of this kind the horizontal section has the shape of a rectangle with rounded corners. At the tuyere level the long

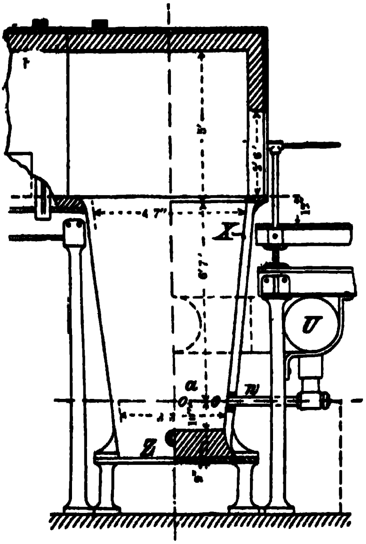

FIG 318.

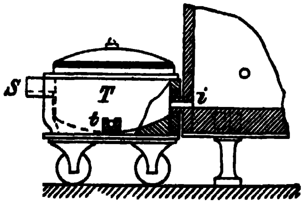

FIG. 319.

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[1] See also vol. i. Figs. 90 and 91.

side is 6 feet, the short side 3 feet. The tuyeres are twelve altogether, five in each long side, one in each short side. The height of this furnace from tuyeres to mouth is about 6½ feet.

The working is carried on just the same as in the smelting of roasted copper ores. The products are matte and slag. If the charge contains much iron, iron sows will form containing a considerable quantity of nickel. The matte contains from 3·5 to 25 per cent. of nickel, according to the nature of the original ore, and the sort of roasting it had; the smallest proportion, 3·25 per cent., being found in the matte formerly produced at Kragerö, in Norway,[1] where the ores were smelted without roasting.

At Klefva in Sweden,[2] the ores had the following composition :—

	First quality. Percentage.		Second quality. Percentage.
Ni	2·03	. .	1·08
Co	0·10	. .	0·07
Fe	57·68	. .	43·24
Mn	0·12	. .	0·20
Cu	0·38	. .	1·03
S	33·52	. .	24·45
SiO_2	0·40	. .	14·75
Al_2O_3	0·20	. .	4·32
CaO	0·12	. .	2·73
MgO	0·09	. .	2·04

The matte produced contained :—

	Percentage.
Ni	4·70
Cu	2·30
S	31·05
Fe	61·95

The matte obtained at Sagmyrna from similar ores contains 5 per cent. nickel.

The magnetic pyrites used at the Ringerick Works,[3] Norway, contains from 0·42 to 1·75 per cent. nickel, and the matte formed from it from 5 to 6 per cent. nickel, and from 3·6 to 3·8 per cent. copper. According to Schweder[4] the composition of the matte is :—

	I.		II.
S	26·5	. .	28·30
Fe	59·62	. .	55·30
Ni	5·7	. .	6·01
Cu	3·65	. .	3·80
Residue	3·88	. .	5·92

At the Sesia Works the pyrites contained 2·2 per cent. nickel, the matte 7 per cent.

At the Isabella Works at Dillenburg the ore formerly used, which consisted of iron pyrites containing nickel, copper pyrites and serpentine, contained 3 per cent. nickel and 5 per cent. copper; the matte had the following composition:—[1]

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[1] Balling, *Metallhüttenkunde*, p. 570, and above, p. 520. [2] *Ibid.* p. 568.

[3] Schweder, *B. und H. Zeitung*, 1879, pp. 18, 79, 106, 122.

[4] Schweder, *B. und H. Zeitung*, 1878, p. 423.

	Ni.	Cu.	Fe.	S.
I.	19·44	22·30	35·20	22·00
II.	14·30	14·92	44·90	26·04
III.	18·11	13·39	42·46	26·04
IV.	13·03	16·55	42·80	27·82

At Sudbury, at the present time, the matte contains 15 to 25 per cent. nickel.

The specimens of this matte sent to the Chicago Exhibition contained—[2]

Ni	18—25	per cent.
Cu	20—25	,,
Fe	25—35	,,
S	20—30	,,

Ahn[3] gives the composition of a Sudbury matte as

Ni	15·5	per cent.
Cu	27	,,
Fe	30	,,
S	26	,,
Co, Pt, Ag, Au	1·5	,,

Sulphur in nickel matte forms protosulphides with copper and silver (Cu_2S, Ag_2S), and monosulphides with nickel and iron (NiS, FeS). If, as is often the case, there is not enough sulphur to form these two latter sulphides, the excess of the metals is dissolved in their monosulphides when in the molten condition; this is according to Schweder's researches.[4] On cooling they separate out. According to Schweder the existence of any sub-sulphides of nickel and iron is improbable.

The composition of the slags lies between mono- and bi-silicates, as already mentioned; and it may even decrease in proportion of silica to a mixture of sub- and mono-silicate. With good management slags contain so little nickel that they can be thrown away. The author can offer only a very few complete analyses of slag.

A slag formerly produced at the Isabella Works had the following composition:—[5]

SiO_2	38·56	per cent.
Al_2O_3	7.61	,,
FeO	35·64	,,
CaO	13·55	,,
MgO	4·79	,,

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[1] Schnabel, *Preuss. Zeitschr.* 1866, p. 106.

[2] V. Ehrenwerth, *Das Berg. und Hüttenwesen auf der Weltausstellung in Chicago.* Wien, 1895.

[3] V. Ehrenwerth, *loc. cit.*

[4] Schweder, *Berg. und Hütten. Zeitung*, 1878, p. 409.

[5] Kerl, *Metallhüttenkunde*, p. 542.

The proportion of nickel is not given; it is said to have been very small and only mechanically enclosed in the form of matte.

The slag at the Ringerick Works in Norway contained 0·108 per cent. Ni, and 0·08 per cent. Cu according to Schweder.[1]

The slag at Sudbury is said to possess a composition between mono- and sesqui-silicate, and to contain 0·45 per cent. Ni and 0·4 per cent. Cu. One specimen contained 38 per cent. SiO_2, 43 per cent. FeO, 4·5 per cent. CaO, 10 per cent. Al_2O_3, 2 per cent. S, 0·45 per cent. Ni, 0·4 per cent. Cu, and 2·5 per cent. MgO.

These slags are partly thrown away, partly added again in similar smeltings, or in the concentration processes for the matte.

The iron sows are chiefly composed of metallic iron, mixed with nickel and copper, and also with sulphur, carbon, silicon, arsenic and antimony compounds. Iron and nickel are present, owing to the reduction of their oxides, or by separation from the fused matte, which contains great excess of these metals.

An iron sow from Dillenburg contained :—

Ni	4·85 per cent.
Cu	1·40 ,,
Fe	88 17 ,,
Co	0·05 ,,
S	4·05 ,,
SiO_2	2·11 ,,

One from the Ringerick Works Schweder gives as having :—

S	10·34 per cent.
Ni	18·11 ,,
Cu	2·7 ,,
Fe	68·85 ,,

If nickel is to be extracted from these sows, they are exposed to a blast on hearths, or smelted in reverberatory furnaces with metallic sulphides, or worked up by wet methods.

EXAMPLES OF THE SMELTING OF ROASTED ORE INTO MATTE

At the Isabella Works[2] the ores were roasted in kilns; they contained before roasting 3 per cent. Ni and 5 per cent. Cu, the gangue being calc spar and diorite. They were worked into matte in a low blast furnace, 5 feet high, 2 feet 4 inches broad, and 2 feet 4 inches deep, which was constructed as a *spurofen* with double slag notches (the so-called *brillenofen*), with one tuyere in the back wall, and was worked "with a nose." The pressure was from 0·6 to 0·65 in. of mercury. The charge consisted of 100 parts roasted ore and 63 of ore slag. In 24 hours 2·2 tons of roasted ore were smelted. The consumption of coke was 70 per cent. of the matte produced. Out of 100 parts ore, 30 of matte were obtained with from 13 to 19 per cent. Ni. The composition of the slag is given above.

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[1] *Loc. cit.*

[2] Schnabel, *loc. cit.*

At Klefva, in Sweden,[1] the ores above mentioned with from 1·08 to 2·3 per cent. Ni, after a previous roasting in heaps, were smelted in *sumpf* furnaces with five tuyeres, coke and wood charcoal being the fuel. The furnaces had an oblong horizontal section about 4 feet broad by 3 feet 3 inches deep. The forehearth extended 3 feet beyond the breast of the furnace. The height of the coke furnace was 12 feet 6 inches, that of the wood charcoal furnace 19 feet 6 inches. The charge was roasted ore and a little unroasted, impure ore-slag, and slag from the concentration of matte. In 24 hours 34 tons of charge were worked. Out of this, 6·3 tons of matte were obtained, containing 4·7 per cent. nickel. There are no figures given for fuel consumption. The length of a campaign is 2 months when coke is used, 6 months with wood charcoal. According to Badoureau, at Sagmyrna in Sweden,[2] the ores contained in the unroasted state 0·6 per cent. of nickel and 0·7 per cent. of copper; they were roasted in heaps and then smelted in furnaces, of which the horizontal section was a trapezoid, 13 feet 6 inches in height (12 feet 6 inches from the level of the tuyeres to the mouth), and 3 feet 2 inches across from front to back. The number of tuyeres was 5, three in the back wall, and one in each side wall. (The other measurements, the blast-pressure and the type of furnace are not stated in the original paper). In 24 hours 10 to 12 tons of ore were smelted, but the consumption of fuel is not stated. The resulting matte contains on the average 4 per cent. of nickel and 4·5 per cent. of copper.

At the Ringerick Works,[3] the raw ore contained on the average 1·73 per cent. of nickel, 0·81 per cent. of copper, and 30 per cent. of gangue. It was roasted in heaps, and smelted in shaft furnaces 6 feet 6 inches high, 3 feet 3 inches deep, 3 feet 3 inches wide, constructed as *sumpfofen*, with 3 tuyeres (1 in the back, 1 in each side); the matte contained from 5 to 6 per cent. of nickel, and from 3·6 to 3·8 per cent. of copper. The charge contained:—100 parts roasted ore, 25 parts slag, 21 parts coke.

The quantity put through and the pressure are not given. A campaign lasted three weeks. After this time the bed of the furnace was so thickly encrusted with sows of iron that the work had to be suspended until they were removed.

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[1] Balling, *Metallhüttenkunde*, p. 566.

[2] *Berg. und Hütten. Zeitung*, 1878, p. 186.

[3] Schweder, *loc. cit.*

At Kragerö, in Norway,[1] ores which unroasted contained 1·25 per cent. Ni were smelted in blast furnaces about 8 feet high, refinery slag being added to them (slag from the refining of the matte), and the product resulting contained 3½ per cent. of nickel.

At the Sesia Works (Varallo in Piedmont)[2] the ores are siliceous, and contain from 1·2 to 1·44 per cent. of nickel. They are smelted in *brillenöfen*, 6 feet 6 inches high, 20 inches wide, and 24 inches deep, with one tuyere in the back, 2 inches diameter at the nose, with a wind pressure of 1¾ in. mercury. The matte contained 7 per cent. of nickel. In 1878 the charge consisted of:—100 parts roasted ores, 28 parts limestone, 25 parts clay, 27 parts slag from the concentration or refining process; 15 parts coke are used to 100 parts charge. In 24 hours 5·4 tons of charge are put through. 100 parts ore gives 32 matte, and 150 slag.

At Sudbury[3] the ores contain on the average 3 per cent. of nickel, and undergo a single roasting in heaps. They are then smelted in Herreshof water-jacket furnaces, round or elliptical, constructed as *spuröfen*, and provided with a movable fore-hearth running on wheels. These furnaces are from 6 feet 6 inches to 10 feet high from the tuyeres to the mouth. To the ores is added a slag containing nickel from the Bessemerising of the matte. The product contains from 15 to 25 per cent. of nickel, and from 20 to 27 per cent. of copper. The water jacket keeps the temperature so low that the formation of iron sows is much diminished or altogether avoided.

At the works of the Canadian Copper Company[4] 125 tons of ore are smelted in 24 hours in Herreshof furnaces about 9 feet high, 6 feet 3 inches in the longer side, and 3 feet 3 inches in the shorter side, at the level of the tuyeres. The consumption of fuel is 15 per cent. The roasted ore has such à composition that no additions are necessary. The 15 tons of matte obtained contains from 20 to 25 per cent. of copper, from 18 to 23 per cent. of nickel, and from 20 to 30 per cent. of sulphur. From selected rich ores a matte is frequently obtained with 52 per cent. of nickel.

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[1] Dingler, vol. 229, p. 376.

[2] Badoureau, *Annales des Mines*, 1877, p. 237. *Berg. u. Hütten. Zeitung*, 1878, p. 186.

[3] Knut Styffe, *Oesterr. Zeitung*, 1894, p. 309. Ehrenwerth, *loc. cit.* p. 368.

[4] *Mineral Industry*, p. 459, 1894. *Trans. Amer. Inst. Mining Engineers*, 1889. Levat, "Mémoires sur les Progrès de la Métallurgie du Nickel," *Ann. des Mines*, 1892

b. THE REMOVAL OF IRON FROM THE COARSE MATTE, OR ITS REFINING

If the matte contains copper, it is worked up into a copper-nickel alloy, or into nickel oxide, or into nickel; if it is free from copper it is worked up into nickel oxide or nickel. In either case the material must first be freed from iron and converted into a nickel-copper matte without iron, or a nickel matte free from iron.

The latter is completely roasted, and either sent into market in that condition, as nickel oxide, or the oxide converted into metal by reduction.

If the nickel-copper matte is to be used for alloys, it is completely roasted and then reduced. But if it is to be converted into oxide for the production of pure nickel, it must be first treated to free it from copper, then completely roasted, and the oxide reduced to metal, or else the roasted product sent to market as it is.

When the coarse matte is poor in nickel, or in nickel and copper, it may be necessary to go through concentration processes first, and in these processes some of the iron may be removed at the same time.

We must then distinguish:—

i. The conversion of coarse matte containing copper into copper-nickel matte.

ii. The conversion of coarse matte free from copper into fine nickel matte.

Most ores contain copper, and therefore produce copper-nickel matte. As a rule it is converted into a fine copper-nickel matte, which can be used to make alloys. But if from this matte a nickel or nickel oxide free from copper is to be obtained, special processes are necessary. They are to be found below.

i. THE CONVERSION OF COARSE MATTE CONTAINING COPPER INTO FINE COPPER NICKEL MATTE

This conversion, the so-called "refining" of the matte, entails smelting with oxidation in ore hearths, reverberatory furnaces, or Bessemer converters (to get rid of iron). If the matte is too poor to be subjected to refining at once (as is the case with the Scandinavian products), refining is preceded by concentration or enrichment, during which a great portion of iron is removed. Such concentration entails roasting followed by smelting in shaft furnaces, or more rarely in reverberatory furnaces; or sometimes a simple smelting in reverberatory furnaces without preliminary roasting. We further distinguish

a. Concentration processes performed on poor matte.

β. Refining of the matte, original or concentrated.

a. CONCENTRATION OF POOR MATTE

This consists in an oxidising roasting, followed by a smelting of the product with coal, and bodies containing silica, in blast-furnaces, or in reverberatory furnaces; or else in a single operation only—an oxidising fusion in a reverberatory furnace. The roasting must be conducted so that in the subsequent reduction the greater part of the iron passes into the slag, leaving the whole of the nickel and copper and part of the iron in the matte. The nickel and copper content of this should be enriched as far as is possible without slagging any considerable amount of nickel. Only most exceptionally is the concentration process repeated on this product.

aa. Roasting the Coarse Matte

This roasting can be conducted in heaps, stalls, shaft furnaces, reverberatory furnaces or muffle furnaces.

The chemical changes are the same as on roasting the ore. The product consists of a mixture of nickel monoxide, cupric oxide, ferric oxide and magnetic iron oxide, undecomposed sulphides and small quantities of sulphates.

Roasting in heaps has the disadvantages already detailed under roasting of ore. The gaseous products are discharged into the air, and as repeated operations are required, much valuable capital is thus compelled to lie idle. It has the advantage that the roasted product passes into the blast furnace in large pieces. It is best if carried on in sheds protected by a roof, to avoid the washing away of nickel and copper sulphates by rain. The operation is conducted similarly to ore roasting; but as the amount of sulphur is smaller, and the amount of foreign minerals to be got rid of is less, the heaps are also smaller than ore-heaps (from 50 to 200 tons). For a complete desulphurisation of the matte 3 or 5 burnings are usually required. In the last one combustible material (wood and wood charcoal) is laid in layers in the heaps, to obtain sufficient heat. The well roasted part of the ore is picked out after each burning, the superficial layers and the badly roasted parts, after the pieces are broken up, are, taken with badly roasted ore from other heaps to a new heap. The bed of the heap is made of brushwood, and coal, or of billets of wood. The heaps burn several weeks or months, according to their size and the amount of sulphur in the matte.

Such roasting in heaps can take place only in places where the noxious gases may be passed into the air, and where sulphuric acid has no value. Such was the case in Sweden and Norway.

Roasting in stalls is not cheaper than in heaps, and endangers the health of the worker when the stalls have to be emptied. Nevertheless with a right management of the air-supply it can be carried on more quickly than the other method, and it possesses this advantage that all noxious effects of the gases can be lessened or removed by the use of high chimneys. By this method, too, the roasted matte enters the furnace in large pieces. Here again several burnings are necessary if the sulphur is to be completely got rid of.

These stalls have been used in Sweden, Norway and Piedmont. In Klefva[1] each holds 50 tons matte. The roasting lasts 5 or 6 weeks. In Sagmyrna (Sweden) a stall holds 25 tons, and the matte goes through four or five burnings.

In the Sesia works at Varallo[2] the matte is roasted four times in stalls, in charges of 20 tons. Each roasting lasts 5 to 8 days. At the last roasting coke is introduced in layers. One ton of wood is used to roast 20 tons of matte.

At the Scopello works in Piedmont[3] there are Wellner stalls for this roasting of matte. These are stalls without a grate, but with a sloping bottom, which has fireplaces in one of the narrower sides. The length of a kiln is from 8 to 10 feet inside, width 10 to 11½ feet.[4] It has four fireplaces, and holds about 25 tons of matte. The matte at these works requires two to four burnings. The roasting of one charge lasts 15 hours.

Roasting in shaft furnaces is suitable when the gases have to be rendered innocuous, or can be converted into sulphuric acid. The necessary condition is that the matte should not sinter easily. In that case the roasting of this matte can be carried on in kilns in a similar way to the roasting of copper and lead matte. Up till now this method of roasting has not been used.

Roasting in reverberatory furnaces is the best way if the gaseous products can be ignored. The roasting is completed in the shortest time, and it can be stopped at the exact point. Nevertheless, it has the drawbacks that there is a comparatively large consumption of fuel, and that the matte must be in small pieces, and therefore passes in this form into the blast furnaces for smelting. The noxious effect of the gases is diminished by the use of very high chimneys.

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[1] Balling, *loc. cit.*

[2] Badoureau, *Berg. und Hütten. Zeitung*, 1878, p. 186.

[3] Badoureau, *loc. cit.*

[4] See vol. i. p. 42.

The same sort of reverberatory furnaces that are described in Vol. I, for the roasting of copper matte, are suitable for this roasting. Such a method was used at the Isabella works at Dillenburg.[1]

The matte there contained from 13 to 20 per cent. Ni, from 16 to 23 per cent. Cu, and from 22 to 27 per cent. S. It was roasted in hand-worked short reverberatory furnaces of the form and dimensions of the lower portion of the old double Mansfield furnace. A charge of half a ton was roasted in 10 hours; for this half ton one-fifth of a ton of coal was needed, and 71 per cent. of the sulphur was got rid of in the roasting.

The roasting is carried on with greater advantage in long-bedded calcining furnaces, and mechanical calciners, than in those of the ordinary type.

Muffle furnaces facilitate the use of the gases for sulphuric acid manufacture; but, like reverberatory furnaces, entail a preliminary reduction of the matte to small size, and a large consumption of fuel. Up till now they have not been used for this purpose. They would be suitable if the gaseous products were to be utilised, and for a matte that sinters easily and so does not lend itself to roasting in a shaft furnace.

bb. Smelting of Roasted Coarse Matte into Concentrated Matte

This smelting is carried on in blast furnaces or reverberatory furnaces. It consists in the smelting of oxides, sulphates and undecomposed sulphides of the various metals. Reverberatory furnaces are used in England; the others in Scandinavia and on the continent. Reverberatory furnaces have this advantage, that there is no formation of iron sows.

Smelting of Roasted Matte in Blast Furnaces

The furnaces are of the same type as for ore smelting. They must not be too high, as otherwise the reducing action of the carbon monoxide is too powerful, so that sows are formed. To decrease the probability of sows the furnace is arranged as a *spurofen*, generally a double gutter furnace with two eyes, the so-called *brillen-ofen* or spectacle furnace. The fixed fore-hearth and the crucible arrangement are both conducive to the formation of sows.

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[1] Schnabel, *loc. cit.*

For the slagging of the iron, acid slag from the working of the ore is added, or quartzose ore, or ore mixed with acid silicates in such a way that a monosilicate slag results. The blast pressure is 0·6 to 1·2 in. mercury. The chemical changes are just the same as in the smelting of roasted ore, except that there is no earthy matter to pass into slag.

The products are concentrated matte, slag, and frequently iron sows as well. If this concentrated matte is still poor in nickel, as used to be the case at some of the Scandinavian works, the processes of roasting and smelting must be repeated. In this repetition the iron, down to a small fraction, is separated from the matte, and this latter is dead roasted and afterwards converted into copper-nickel. This method of getting a matte free from iron is, however, unsatisfactory in its results, takes up much more time, and is more costly than the refining of the concentrated matte described below.

At Dillenburg, at the Isabella works, the coarse matte contained from 13 to 19 per cent. Ni, from 14 to 22 per cent. Cu, and from 35 to 44 per cent. Fe. The concentrated matte obtained from it had the following composition:—[1]

	I.	II.	III.
Cu	34·49	35·68	49·66
Ni	28·60	32·93	30·19
Fe	15·58	13·03	9·24
S	21·15	18·17	10·91

At Klefva, in Sweden, the concentrated matte contained from 52 to 57 per cent. Ni; 22 to 28 per cent. Cu.

At Sagmyrna, in Sweden, its composition was: from 25 to 26 per cent. Ni, from 25 to 30 per cent. Cu, 26 per cent. Fe, and from 25 to 30 per cent. S.

At Kragerö, in Norway: 30 per cent. Ni, and 15 per cent. Cu.

At Sesia works, Piedmont: from 28 to 32 per cent. Ni, from 48 to 52 per cent. Fe, and 20 per cent. S.

At St. Blasien: from 24 to 26 per cent. Ni.

In such concentrated matte nickel and iron exist partly as monosulphides, partly as separated metals dissolved in these. In the cooling of the fused matte the metals frequently separate out in large crystals. A very poor concentrated matte was produced at the Ringerick works, in Norway.[2] The original coarse matte contained 5 or 6 per cent. nickel; the concentrated, from 10 to 12 nickel and from 7 to 10 per cent. copper; apparently this resulted from very incomplete roasting of the matte. According to Ebermayer the slag from the concentration process from the Aurora works at Gladenbach had the following composition :—[1]

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[1] Schnabel, *loc. cit.*

[2] Schweder, *loc. cit.*

Silica	39·368
Alumina	9·696
Ferrous oxide	36·859
Cupric oxide	0·521
Nickelous oxide	1·137
Magnesia	6·871
Lime	5·865
Potash	0·207
Soda	0·994

A specimen of the slag at Klefva had this composition :—[2]

Silica	28·09
Alumina	3·50
Ferrous oxide	60·52
Cobaltous oxide Nickelous oxide Manganous oxide	1·44
Sulphur	0·58

This slag is added to the ore in ore-smelting to recover the nickel contained.

The iron sows have a similar composition to those formed in ore smelting. One at the Ringerick works contained 20 per cent. nickel and 1·5 per cent. copper. These are put in with the ore in ore smelting, or worked upon the refining hearths.

At Klefva, in Sweden,[3] the coarse matte was roasted in stalls. It contained before roasting from 3 to 4 per cent. of nickel; it was smelted in a blast furnace about 5 feet high, with one tuyere in the back wall. The product contained from 45 to 57 per cent. of nickel; the coke used was 25 per cent. of the roasted coarse matte: quartz was added to the charge.

At the Ringerick nickel works in Norway the coarse matte contained from 5 to 6 per cent. of nickel. It was smelted in blast furnaces 6½ feet high, and gave a concentrated matte with from 10 to

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[1] Schnabel, *loc. cit.*

[2] Kerl, *Metallhüttenkunde*, p. 543.

[3] Balling, *loc. cit.*

12 per cent. nickel, and from 7 to 10 per cent. copper. The charge was:—

100 parts	Roasted matte.
25 „	Slag.
6 to 7 „	Sand.
.5 „	Lime.
22 „	Coke.

The campaigns of the furnace lasted only 8 to 10 days, owing to the formation of iron sows rich in nickel (19 or 20 per cent.). At Kragerö, in Norway,[1] the original matte contained from 3 to 4 per cent. of nickel; after roasting it was smelted in a blast furnace about 4 feet 3 inches high, 38 inches wide, and 25 inches deep. The concentrated product contained 30 per cent. of nickel and 15 per cent. of copper. This matte was roasted and then smelted in the same furnace, and was converted into a matte with 60 per cent. Ni, 30 per cent. Cu, and 10 per cent. S. This last was completely roasted, and smelted to copper-nickel.

At the Sesia works at Varallo,[2] Piedmont, the raw matte contained 7 per cent. of nickel and cobalt; it was smelted in a blast furnace with the addition of 42 per cent. quartz, and the product was a matte with from 28 to 32 per cent. Ni, from 48 to 52 per cent. Fe, and 20 per cent. S. The daily output was 8·5 tons; 100 parts coarse matte gave 22 parts concentrated. To get 100 parts of the latter 17·5 parts of coke were used (dimensions of furnace not given).

At the Isabella Works in Dillenburg the original matte contained from 13 to 19 per cent. of nickel, and was roasted in reverberatories. It was smelted in blast furnaces to a concentrated matte, with from 28 to 30 per cent. Ni, and from 34 to 49 per cent. Cu. The furnaces were low blast furnaces, with one tuyere in the back wall, 5 feet high, 2 feet 4 inches wide and deep, arranged as "*brillenofen.*" The blast was 1·6 inches mercury. The campaigns lasted from 14 days to 3 weeks. From 100 parts coarse matte 32 parts concentrated matte used to be obtained. In 24 hours 1·25 tons of the roasted matte was put through. The quantity of coke is 55 per cent. of coarse matte; this is very high, and is caused by the low furnace.

Smelting Roasted Matte in Reverberatory Furnaces

These reverberatory furnaces are arranged just as those for the concentration of copper matte after the English method.[3] To the roasted matte there is added a certain quantity of quartz, or glass, to slag the iron. The iron is partly slagged by the action of the quartz lining of the hearth.

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[1] Dingler, vol. 229, p. 376.
[2] Badoureau, *loc. cit.*
[3] *Vide* vol. i p. 129 *et seq.*

The chemical changes in the smelting of the roasted matte, already referred to, are as follows. Ferric oxide is reduced to ferrous oxide by the undecomposed sulphide of iron present; this passes into the slag, and sulphur dioxide is formed; a further quantity of sulphide of iron is changed to ferrous oxide by the nickel and copper oxides, and also slagged, the oxides of these metals meanwhile becoming sulphides; further copper oxide and undecomposed copper sulphide give metallic copper and sulphur dioxide. This copper is reconverted into sulphide at the expense of some iron sulphide. The iron thus separated is partly taken up by the matte, partly acts upon a corresponding amount of ferric oxide, giving more ferrous oxide to be slagged. There is no action between nickel oxide and sulphide. The various metallic sulphides unite to form the concentrated matte.

This method of concentration was formerly used at Sagmyrna, in Sweden, where the matte, containing from 13 to 14 per cent. of nickel, was first treated with dilute sulphuric acid to separate some of the iron; then roasted, and smelted in reverberatories with a quartz flux, giving a matte of 35 per cent. Ni, 40 per cent. Cu and 0·4 per cent. Fe

The Oxidation of Coarse Matte in Reverberatory Furnaces

This is done in the same manner as the oxidising of copper matte in England. The unroasted matte is charged in a reverberatory furnace on a sand bed, and first subjected to a partial roasting, which removes part of the sulphur and oxidises the iron; then the temperature is raised and the whole smelted with the addition of sand. The iron passes into the slag, and the nickel and copper present form a matte. The process is finished when samples from the furnace show that the greater part of the iron has been removed. It lasts about 8 hours. In England a furnace produces 2 tons of matte daily, with consumption of 2 tons of coal. Matte is obtained with only from 2½ to 3 per cent. of iron. The slag contains from 2 to 2½ per cent. of nickel. This is added to first ore-smeltings. By the repetition of the oxidation (which may be looked upon as the refining of the matte) the proportion of iron is brought down to 0·5 or 0·75 per cent.[1]

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[1] Levat, *Ann. des Mines*, 1892, Bk. 2, pp. 141—244.

β. THE REFINING OF THE COARSE MATTE OR THE CONCENTRATED MATTE

The refining of the matte with sufficient content of nickel consists in an oxidising fusion, by which the iron sulphide is converted into ferrous oxide and slagged off. Iron may also be removed by roasting, followed by reduction in a blast furnace, or by repetition of these operations. But this latter method is lengthy, expensive and less complete than the purifying by oxidising fusion. Also iron can be removed by roasting the matte, and smelting the product in reverberatory furnaces. But this way is also more expensive than the simple oxidising fusion of unroasted matte.

The smaller the quantity of iron to be removed from the matte, the quicker and the less attended by loss is the oxidising fusion Samples with less than 16 per cent. of nickel are rarely subjected to this process, and, if it was desired to prevent great loss of nickel in the slag, would give a matte still containing an appreciable quantity of iron, which would necessitate a second purification.

The plant for the oxidising fusion consists of hearths, converters or reverberatory furnaces. In hearths only small quantities of matte can be worked. The use of them renders a large consumption of fuel and labour necessary. They have been used in Scandinavia and on the Continent, but have fallen into disuse owing to these drawbacks.

Converters permit the working of large quantities of matte in the shortest time, and need only a very small quantity of fuel to fuse the matte (if this is not run directly into the converters in the liquid state from the furnaces in which it is produced), and, further, they ensure a more complete separation of arsenic and antimony than hearths and reverberatory furnaces. But they demand a blast with high pressure, and much fire-proof material for lining and renewing linings, whilst, during the operation, large quantities of sulphur dioxide are set free, which it is most difficult to prevent being noxious.

In spite of these objections they are preferred to reverberatory furnaces, wherever power is cheap, impure mattes have to be treated, and fuel is dear whilst refractory materials are cheap. They are used with good result at Sudbury, in Canada, and on the Continent.

Reverberatory furnaces can be managed more cheaply than hearths, and use raw fuel. The gases produced are comparatively poor in sulphur dioxide, and can be rendered harmless by passing into high chimneys. They are used where converters are not convenient from the noxious nature of their gases, or from not being adapted for small production; and where coal is very cheap. They are specially used in England.

The chemical changes in these various arrangements are the same, only they take place more rapidly in the converters than in the other forms.

The iron is converted into ferrous oxide by the oxygen of the air, and slagged by the silica of the furnace lining, or by siliceous matters added. Besides the iron a certain amount of nickel and of copper is oxidised, to the lower oxide in each case. Nickel monoxide with iron sulphide forms nickel sulphide and ferrous oxide. Cuprous oxide and copper sulphide form copper and sulphur dioxide, cuprous oxide and iron sulphide form copper sulphide, iron, ferrous oxide and sulphur dioxide. Separated copper takes sulphur from any iron sulphide remaining, and sets iron free, which passes into the matte.

Finally there results a matte of nickel and copper sulphides with only a fraction of a per cent. of iron.

Refining of the Matte in Hearths

The hearth is constructed exactly like the small refining hearth used for copper.[1] It consists of a cavity, hollowed in powdered quartz or sandstone, hemispherical in shape, and over it is a chimney-hood. It contains according to size from 1½ to 5 cwt. of matte. In front of the hearth there is generally a small slag hearth, in which the slag from the former collects. The nickel-copper matte is either run off by a tap-hole in the deepest part of the hearth into a cavity in front, or else taken out of the hearth after cooling. There is one tuyere in the back wall of the hearth; it has an inclination of from 22° to 32°.

At the Isabella works the hearth of powdered sandstone was about 14½ inches in diameter, 8½ inches deep.[2] The charge was 187 lbs. The pressure was 1·2 inches mercury.

After the hearth was properly dried by wood charcoal, the concentrated matte was melted with coke. After the lapse of 1¾ hours the melting was complete. The fuel was then removed, and the slag floating on the surface of the matte blown cold and removed. Again fuel was piled up, and the oxidising blast used until again a certain quantity of slag had collected, when it was removed in the same way. The indication that iron was wholly removed from the matte was the appearance of an enamel-like lustre in the solidified slag: this generally appeared ¾ hour after complete fusion. The working of one charge lasted 2½ hours. After the stoppage of the blast the nickel-copper matte was run into a cavity, lined with brasque, in the bottom of the hearth, whereby it took the form of a slab 4 feet 3 inches long, 1 foot broad, and 2 inches thick. On the average 13½ cwt. of matte were blown in 24 hours. Out of 100 parts concentrated matte (with from 28 to 32 per cent. Ni and from 34 to 49 per cent. Cu) there were obtained 62 parts nickel-copper matte with from 39 to 42 per cent. Ni and from 40 to 42 per cent. Cu. For 100 parts of this latter, 72 of coke were required, and two men worked one hearth. The approximate composition of the nickel-copper matte is to be seen from the following analyses by Fresenius:—

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[1] Vol. i. p. 171.

[2] Schnabel, *loc. cit.*

	I	II	III
Cu	42·81	44·70	40·72
Ni	40·97	39·68	42·38
Co	0·26	0·64	0·78
Fe	0·23	0·20	0·48
Sb	0·04	0·90	1·22
As	0·16	0·07	0·04
S	15·19	13·55	13·95
Residual matter	0·04	0·02	0·14

This matte consisted of a mixture of metallic sulphides and metals, the latter including arsenic and antimony. It may be seen that the iron is reduced to a mere fraction per cent. It is hardly wise to attempt to remove this last trace, as a considerable quantity of nickel would thus be slagged off.

Further, arsenic and antimony remain in appreciable proportion in this matte. The refining slag contains nickel, partly chemically combined, partly mixed mechanically, on account of its high specific gravity.

The composition of such a slag at the Aurora Works at Gladenbach, where refining is carried on in the same way as at Dillenburg, is shown by the following analysis by Ebermayer:—

SiO_2	36·291
Al_2O_3	10·710
FeO	48·690
CuO	1·074
NiO	2·142
CoO	0·262
MgO	0·309
CaO	0·680
Alkali	Traces.

At the Isabella Works the loss of metal in refining was 19 per cent. of copper and 4·9 per cent. of nickel. These metals were for the most part recovered, inasmuch as the slag is added in smelting ore.

At Klefva,[1] the hearth, made of quartz-sand, took a charge of about 5½ cwt. The tuyere had an inclination of 32°. To slag the iron quartzose sand was thrown from time to time on to the molten charge. Wood charcoal was used as fuel. The refined matte, known as *garstein*, had the following composition:—

Ni	61·06
Cu	30·73
S	7·79
Fe	0·42.

At the Ringerick Works,[2] a poor matte containing only from 10 to 12 per cent. of nickel and from 7 to 10 per cent. of copper was treated in the hearth. The matte resulting contained so much iron that it had to undergo further refining, which was carried on in a reverberatory furnace. The matte refined on the hearth contained:—

Ni	from	40	to	50	per cent.
Cu	„	20	„	30	„
Fe	,	6	„	10	„
S	„	20	„	22	„

Refining of Matte in Reverberatory Furnaces

The reverberatory furnaces for this purpose are constructed like those used in England for refining copper matte. The hearth is made of quartz. Quartz and also some heavy spar are added to slag the iron.

Silica reacts with barium sulphate to form barium silicate and set free sulphur trioxide, decomposed into the dioxide and oxygen.[3] Oxygen thus formed seems to have a specially marked action on iron sulphide. Since oxidation in a reverberatory furnace is less strong than in hearth furnaces and converters, there is frequently obtained a matte with 2·5 to 3 per cent. iron; in which case the process is repeated. Also arsenic and antimony are not so easily got rid of as they are in hearths, and much less easily than in converters.

The process is generally so arranged that there is at first a somewhat low temperature, as in the roasting fusion of copper matte, so that a sort of roasting of the matte takes place; after the addition of quartz sand, the temperature is raised.

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[1] Balling, *loc. cit.*

[2] Schweder, *loc. cit.*

[3] Schweder, *loc. cit.*

The process is used in England and on the Continent. In England,[1] it is carried on in two operations; the first has already been spoken of under concentration of coarse matte, and yields a concentrated matte with from 2·5 to 3 per cent. of iron. The second operation (refining proper) is conducted exactly like the first (after the principle of the roasting fusion of copper matte), and yields a matte with from 0·5 to 0·75 per cent. of iron. The proportion of sulphur in the refined material must be at least 16 per cent., in order that it may be readily crushed down to the size necessary for the later dead roasting. The length of each operation is about 8 hours. During one day 2 tons of matte are worked up in the furnace, consuming an equal weight of coal. The slag which holds from 2 to 2½ per cent. of nickel is added in a first smelting operation.

At the Ringerick Works, a matte which was at one time refined in reverberatory furnaces after having been purified by a blast contained from 40 to 50 per cent. Ni, from 20 to 30 per cent. Cu, and from 6 to 10 per cent. Fe. To every 100 parts of this *garstein* were added from 45 to 60 parts heavy spar, and from 20 to 30 parts sand. The firing was continued until the evolution of gases, chiefly sulphur dioxide, was finished. Then the slag was drawn off, and the refined matte tapped.

According to Wagner, it is possible to obtain a matte almost free from iron by smelting matte already purified by the blast with a mixture of saltpetre and soda, either in crucibles or in reverberatory furnaces A matte containing 25·32 per cent. Ni, 37·65 per cent. Cu, 10·58 per cent. Fe, and 26·45 S., yielded, when smelted with 15 per cent. mixed saltpetre and soda, a matte with 40·93 per cent. Ni, 58·64 per cent. Cu, 0·25 per cent. Fe, and 0·18 per cent. S. This method appears not to have come into use, for economic reasons.

Refining of Matte in Converters.

The converters are constructed like those for purifying copper-matte by the blast,[2] and, like them, have quartz linings. The openings of the tuyeres at the sides must lie at a certain distance above the bottom. If the blast entered through the bottom of the converter, the nickel-copper matte collected there would soon be solidified. The matte is run directly into the converter out of the furnace in which it was produced, or else melted beforehand in a cupola furnace. The charge in the converter is about one ton of matte; the pressure up to 16 in. mercury. During the blow quartz-sand is added, to slag the iron and save the lining. The length of the blow varies, according to the content of iron, from 25 minutes to 1½ hours.

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[1] Levat, *loc. cit.*

[2] Vol. i. p. 158.

With matte containing 36 per cent. of iron the time of the blow is 1 hour 20 minutes (at the works near Havre). When the proportion of iron has gone down to 0·5 per cent., the blast is stopped and the matte poured. The slag remaining from this process is pasty, and contains from 2 to 15 per cent. of nickel, as well as 2 per cent. of copper, partly as silicates, partly enclosed mechanically. This is returned to the ore-smelting process.

At Sudbury the coarse matte treated in converters contains from 16 to 25 per cent. of nickel, from 20 to 27 per cent. of copper, and from 25 to 35 per cent. of iron. The matte should contain a certain amount of sulphur (16 per cent.) in order that it may be readily broken up for the ensuing roasting.

Attempts to separate metallic nickel by further application of the blast to the matte after the iron has been removed, have been unsuccessful, because nickel, up to a certain stage, is more easily oxidised than sulphur, and because the heat set free by the oxidation of the sulphur is not sufficient to fuse and to keep fused the nickel with its high melting point.

In illustration of the Bessemer method we may quote the Canadian Copper Company's works at Sudbury, and the works at Havre (France).[1] The plant of the former consists of three converters, of which one only is in operation at one time, while a second is being given a new lining, and the third stands ready to start. In this arrangement 25 tons matte, which has been fused in cupola furnaces, is treated in 24 hours, and yields 15 tons refined matte. The iron is almost completely removed, while the proportion of nickel is increased to 40 per cent., and that of copper to 45 per cent. Sulphur is removed, except 5 to 15 per cent. The refined matte is tapped out of the converter and cast into square slabs about 3 inches thick and 3 feet in the side.

There are no special indications in the flame for the disappearance of iron and the commencement of the slagging of the nickel. Normally the slag does not contain more than 2 per cent. of copper and 3·5 per cent. of nickel. The average composition of the refined matte is

Cu	43·36	per cent.
Ni	39·96	„
Fe	0·3	„
S	13·76	„

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[1] T. Ulke, *The Mineral Industry*, 1894, p. 460.

It also contains 7 oz. of silver per ton, 0·1 to 0·2 oz. of gold, and 0·5 oz. of platinum.

At the Havre works[1] the converter holds only 1 ton. The blast pressure is 16 in. of mercury. Quartz sand is added, as soon as the temperature is high enough, to slag the iron. If the content of iron in the matte does not exceed 36 per cent., the operation is over in 80 minutes. If the percentage of iron is larger, it is necessary to tap out the iron slag first formed at the end of 25 minutes, and then continue the blow with the addition of more sand. As soon as the oxidation of nickel begins, the operation is stopped. The refined matte contains 0·5 per cent. of iron. The slag is difficultly fusible and contains 14 to 15 per cent. of nickel, chiefly in mechanically enclosed portions of matte. Part of this latter can be removed from the bottom of the slag-pots in metallic bottoms. The slag is returned to the ore-smelting.

ii. THE CONVERSION OF COARSE MATTE FREE FROM COPPER INTO REFINED MATTE

If the coarse matte is free from copper or contains only a very small quantity of it, there is only the iron to be got rid of, with its equivalent of sulphur. In this case the conversion differs in no particular from the conversion of the coarse matte containing copper into nickel-copper matte. It is just in the same way subjected to oxidising fusion in hearths, reverberatory furnaces or converters, and, when necessary, concentrated in a similar manner before this oxidising fusion. The chemical reactions are also the same, with this exception, that those involving copper and its compounds do not take place. As the occurrence of a sulphuretted nickel ore free from copper is rare, this refining process is rarely carried on. In Europe the operation is at present performed in reverberatory furnaces after the manner of a roasting fusion. This is described for nickel-copper matte on page 541, and need not be repeated. The matte obtained contains roughly 75 per cent. Ni, 24 per cent. S, 0·5 per cent. Fe, and 0·5 per cent other impurities.

c. THE CONVERSION OF NICKEL-COPPER MATTE INTO COPPER-NICKEL ALLOYS

This conversion consists of a roasting to convert nickel and copper into oxides, and a subsequent reduction of the mixed oxides with or without fusion, to an alloy of the two metals.

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[1] T. Ulke, *The Mineral Industry*, 1894, p. 466.

a. ROASTING THE MATTE

It must be dead roasted. To this end it is powdered as finely as possible, and then twice roasted in a reverberatory furnace. Oxidising material, such as saltpetre, is frequently added in the second roasting. Long-bedded calciners, as also short hand-worked reverberatory furnaces, are used for this operation.

At Klefva, in Sweden,[1] one of the former kind, with sloping hearth, was used; it held four roasting charges, of 2½ cwt. each. At Gladenbach,[2] in Nassau-Hesse, a furnace was used with a rectangular hearth about 45 square feet in area, with a single working opening and two flues. The greatest height of the arch of the furnace above the bed was 14 inches: the charge was 4 cwt.

During the first roasting sulphur was removed, down to 1 per cent. The roasted matte was pulverised, and then further roasted to remove the last portion of sulphur The first roasting lasted 6 to 12 hours, the second 6 to 8 hours. According to Levat, the consumption of fuel for 1 ton of refined matte was ⅝ ton of coal in the first roasting, and 1½ tons in the second. The result of the roasting was a mixture of cupric oxide and nickel monoxide, which had a dark grey to black colour according to the proportion of copper.

At the Aurora works at Gladenbach[3] about 4 cwt. of pulverised matte was spread out on the hearth an inch or inch and a half deep, and roasted for 12 hours, with continuous raking through, and occasional turning. To prevent sintering of the material the temperature was lowered at the beginning of the roasting, and not allowed to rise above dull redness until the end, when it was brought to a bright redness. Sulphur was removed in this first roasting down to ¾ per cent.

The product was powdered and then subjected to an 8 hours roasting in the same furnace with the addition of saltpetre and soda. At first the temperature was raised to a bright redness, but finally brought to a white heat to completely decompose the sulphates formed. During this second roasting arsenic and antimony were converted into arseniates and antimoniates by the saltpetre and soda, and these were removed by washing with water before further treatment.

At Klefva[4] the roasting was carried on in furnaces with inclined hearth. In these, four charges, each of 2½ cwt., were put through. Wood was used as fuel. In the first roasting, one charge (2½ cwt.)

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[1] Balling, *loc. cit.*

[2] Schnabel, *loc. cit.*

Schnabel, *Preuss. Ministerialzeitschrift*, 1866, p. 137.

[4] Balling, *loc. cit.*

was put through in about 4 hours; in the second roasting, in the space of about 8 hours.

At the Ringerick works in Norway[1] sulphur was removed down to 2 or 4 per cent. in the first roasting. In the second, 10 per cent. by weight of calcined soda and 5 per cent of saltpetre were added to the already roasted matte. The salts thus formed were leached out by water from the product.

According to Levat the refined matte is completely roasted in two operations in the new works in England and on the Continent. During the first, sulphur is removed down to 1 per cent., in the second at the most only 0·004 per cent. remains. The first operation is carried on in a long-bedded calciner 33 feet long and 8 feet broad with four working doors in the long side. The matte, crushed between rolls, is put into the furnace in charges of about 16 cwt., and spread on the bed to a depth of two inches. The temperature at first is kept down to dull redness to avoid sintering, and raised to bright redness at the close of the operation. The product is drawn out at the firebridge. The length of the operation is about 6 hours for matte containing copper, and 8 hours if free from copper, as the nickelous sulphide is more difficult to decompose than copper sulphide. The quantity put through in 24 hours is 2½ tons for first charge, or 36 cwt. for second, with a fuel consumption of 2 tons of bituminous coal. The furnace is tended daily by three men.

The product, which contains about 1 per cent. sulphur due to the presence of undecomposed lower sulphides and basic salts, is crushed as fine as possible by rolls, sieved, and put for a second roasting into a furnace as wide as that described last, but much shorter. The charge is half a ton of the preceding product, which is completely roasted at a bright red heat in 6 hours. Every 24 hours 3 tons of coal are used. The furnace is tended by two men in a day. The oxide now resulting should not contain more than 0·004 per cent. sulphur. It is black if copper is present, and greenish-grey if it is not.

β. REDUCTION OF COMPLETELY ROASTED NICKEL-COPPER MATTE TO COPPER-NICKEL ALLOYS

The mixture of cupric and nickelous oxide is reduced to a copper-nickel alloy. The process can be carried on, so that either an alloy without fusion is obtained in powder, dust or cubes, or so that the alloy is obtained fused.

Nickel monoxide is reduced at a strong red heat, without being fused at that temperature. Cupric oxide is reduced at a still lower temperature.

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[1] Schweder, *loc. cit.*

The formation of alloy in the form of powder or cubes takes place in muffles, in crucibles, or in tubes, while the production of fused alloy takes place in shaft furnaces.

To make the powder the oxides are mixed with powdered coal and pressed tight in graphite crucibles; to make cubes they are made into a stiff paste with viscid carbonaceous substances (syrup, raw sugar) with the addition of water, made into flat cakes, and lastly divided into little cubes of 0·4 to 0·6 inch side. These are ignited with powdered coal in crucibles or tubes.

To make the fused alloy the oxides are smelted with charcoal in a little shaft furnace

At Klefva[1] the oxides were reduced in the form of powder in graphite crucibles in quantities of about 19 lbs. The crucibles were heated for 12 hours in a wind furnace which held from 8 to 12 pots. The pulverised alloy, which was a commercial product, had the following composition:—

	I.	II.
Ni	60·25	66·46
Cu	38·85	32·33
Fe	0·64	0·70
S	—	0·08

At the Ringerick works the moist oxides were mixed with raw sugar, made into cubes, dried, and placed in crucibles in layers with powdered coal, and kept at a white heat for 5 hours. The cubes obtained were emptied into an iron box, in which they were cooled, then separated from coal by sieving, and finally polished with water in a rotating drum.

At the Victoria works in Silesia[2] the oxides were made into a paste with wheat-meal, then spread out on a copper sheet, divided into cubes and dried. The cubes were placed in layers with charcoal in graphite pots, and these heated in a wind furnace with coke; for one pot yielding about 11 lbs. alloy, 13 to 15 lbs. of coke were needed. (For the reduction of nickel monoxide in muffles see later, p. 551.)

The reduction of the oxides in a blast furnace was formerly carried on at the Aurora works at Gladenbach,[3] and also occasionally at

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[1] Balling, *loc. cit.*

[2] *Berg.- und Hütten Zeitung*, 1877, p. 300; 1878, p. 245.

[3] Schnabel, *loc. cit.*

Klefva. At the former place the blast furnace, arranged as a crucible furnace, was 2 feet high, 1 foot 4 inches deep, and 1 foot 6 inches wide. The sole consisted of a light brasque (4 to 5 parts by volume of wood charcoal, 1 of loam). The blast, at a pressure of 1¼ inches mercury, was given by one tuyere in the back wall, with an average inclination of 45°. Wood charcoal was used for the reduction. As soon as a quantity between 175 and 220 lbs. of oxide was run down, the alloy and slag were tapped out into a little tapping hearth. After the solidified slag was removed from the alloy, the latter was taken off in discs and broken into pieces while still red-hot. Out of 100 parts oxide 35 to 38 parts alloy were obtained.

An easily fusible slag was formed by part of the oxides, the loam of the brasque, and the material of the furnace wall, which slag protected the alloy from being oxidised by the air of the blast. The slag contained considerable quantities of copper and nickel, and had also to be worked up separately for alloy. The loss of metal was 1·35 per cent. Ni and 8·22 per cent. Cu. Out of a refined matte which before roasting had the composition:—

Ni	32·59	per cent.
Cu	52·00	„
Fe	0·41	„
S	17·71	„
As+Sb	0·11	„

an alloy was obtained containing:—

Cu	59·5	per cent.
Ni	39·95	„
Fe	0·64	„

Out of an original matte which when unroasted had this composition:—

Ni and Co	37·5	per cent.
Cu	48·5	„
As and Sb	Trace	„
S	13·3	„

an alloy was obtained containing:—

Ni	45·06	per cent.
Cu	53·44	„

c. THE CONVERSION OF REFINED MATTE CONTAINING COPPER (NICKEL-COPPER MATTE) INTO NICKEL MATTE FREE FROM COPPER

This conversion of the nickel-copper matte into matte free from copper is necessary if nickel monoxide or nickel is to be produced. This latter matte can then be treated in the same way as the refined matte without any copper.

Copper is removed by smelting the matte with sodium sulphate and coal. In this operation any iron present is also removed; therefore the matte may contain a certain quantity of iron. Unrefined or coarse matte with not too large a proportion of iron can also be treated in this way. If the matte contains a small quantity of copper, this can be converted into copper chloride by a chloridising roasting, and the salt so formed can be washed out by water.

The removal of copper by the sulphate of soda and coal treatment depends on the fact that sodium sulphide unites with copper and iron sulphides to form an easily fusible matte, into which nickel sulphide enters merely in small quantities. This matte is of less density than the one containing nickel sulphide, and separates from it on cooling. Any iron or copper present in this new nickel matte is removed by repeating the process. The matte of copper, iron, sodium and nickel sulphides is allowed to weather, and then smelted with coal, together with coarse matte obtained from the original ore; whereby the nickel content of both products is collected into one matte. This latter is smelted with sulphate of soda and coal, and gives, on the one hand, a matte consisting chiefly of nickel sulphide, and on the other, a copper-iron-sodium matte. By mingled repetitions of these operations the whole nickel is finally obtained in a matte of pure nickel sulphide. This is converted into the monoxide by oxidising, and may be sent into market, or reduced to nickel.

In removing copper from matte by chloridising roasting, it is desired to convert the metal as much as possible into cupric chloride, which is soluble in water. The chlorides are dissolved out, and the residue (consisting, if from a refined matte, of nickel monoxide, but usually nickelic oxide also) is smelted with sodium sulphide, sand and wood charcoal. A pure nickel sulphide is thus obtained, and afterwards completely roasted. The nickel monoxide is reduced to nickel.

This method, proposed by Emmens, is only applicable, however, when the quantity of copper is very small. For instance, if the matte contains 20 per cent. copper, Youngwood[1] finds that a great part of it does not combine with chlorine, and thus escapes the removal by water.

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[1] *The Mineral Industry*, 1894, p. 463.

It has also been suggested[1] to remove copper from matte containing both copper and iron by the action of the blast in converters with basic or coke linings. First the iron, and next the nickel, would pass into slag, while the copper in the end would be separated as metal. It is said that the nickel slag can be removed from the converter separately from the iron slag, and worked up alone for nickel by a wet or a dry method. The process would be divided into two periods by the adding of fluxes and slagging materials. In the first period, just as in the present method of working up an iron-copper-nickel matte, the iron would be slagged, and a copper-nickel matte free from iron remain. In the second period the nickel would be slagged and the copper separated as metal. Nothing is known as to the execution of this suggestion.

The method of treating the matte containing copper by sodium sulphate and coal is used at the Orford Copper Company's works at Constable Hook, New Jersey, near New York. The operation has been devised and is practically carried out by John Thomsen, director of the above company, and Charles Bartlett.[2] Since it is kept secret, only incomplete accounts have become public. According to these coarse matte or preferably concentrated matte is smelted with sodium sulphate and coal in a small blast furnace, where the sulphate is reduced to sodium sulphide, which makes the already mentioned fusible compounds with iron and copper sulphides. The products are tapped out into a receiver, at the bottom of which the heavier nickel sulphide collects, with only small quantities of the other two sulphides; while the chief part of these sulphides with sodium sulphide (according to other accounts, with caustic soda) lies on the top, and after solidification can easily be lifted off. The nickel sulphide separated from the upper layer ("tops"), still contains iron and copper, and is treated again in the same way to remove these metals, so that there are again obtained upper layers and a nickel sulphide free from iron and copper. The upper layers after being left for some time to disintegrate, are smelted with coarse matte and coke, and thus again a matte rich in nickel, and the same fusible compound of copper, iron, sodium and sulphur is obtained.

By suitable repetition of these operations a fairly pure nickel matte is apparently obtained. This is oxidised and smelted with the addition of sand, producing a very rich and pure matte. (The authorities quoted do not describe the plant used.)

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[1] Von Ehrenwerth, *Berg.- und Hüttenwesen auf der Weltausstellung in Chicago*, Wien, 1895.

[2] *Mineral Industry*, 1892, p. 357. John L. Thomsen, American patent, No. 489,882, Jan. 10, 1893.

These processes attain their end quite successfully, but appear to be lengthy and costly.

To use the method of chloridising roasting, the great part of the iron should be first removed in a converter. Then chloridising roasting takes place in presence of steam. Cupric chloride is leached out by water from the products. The residue consists of nickel monoxide with a certain quantity of iron oxide. It is smelted with sodium sulphide, sand and wood charcoal into a pure nickel matte.

d. CONVERSION OF NICKEL MATTE REFINED, OR FREE FROM COPPER INTO NICKEL MONOXIDE, OR CRUDE NICKEL

Nickel matte is converted into crude nickel in the same way as nickel-copper matte into the copper-nickel alloy. That is, the matte is completely roasted and the monoxide reduced to nickel. The complete roasting is done in the same manner and with the same apparatus as before, and the account need not be repeated.

In many cases nickel monoxide itself is sent into commerce. The composition of two specimens of this substance, obtained from Canadian ores, is given in the following analyses :—

	Ordinary Monoxide. Per cent.	Better Quality. Per cent.
NiO and CoO	97·5	98·74
CuO	0·4	0·30
Fe_2O_3	1·5	0·70
As	0.3	0·04
S	0·03	0·02
SiO_2	0·3	0·20

The reduction of this compound to nickel takes place in the same way as the reduction of the mixed copper and nickel oxides.

The nickel monoxide is either as above mixed with meal, syrup, sugar, or such carbonaceous bodies, and reduced by wood charcoal at a temperature below the melting point of nickel, whereby the metal is obtained pulverised or in a spongy mass; or else it is reduced at a temperature a little above the melting point, with carbonaceous matter and a slight addition of materials for slagging; then the metal is produced fused, and can be obtained in any desired form.

If nickel in powder, or cubes, or as sponge, is to be produced, crucibles, retorts or muffles are used. The reduction in crucibles is the same as in preparing copper-nickel alloy.

The reduction of the oxide in retorts of fire-clay is described by Künzel,[1] and has been carried out at Val Benoit, near Liége. The retorts are open at both ends, and have a width of 8 inches. They are placed in rows of 6, in a furnace of similar construction to the French one for liquation of antimony at Malbosc.[2] The charging is done through openings in the arch of the furnace, to which openings correspond similar ones in the bed. Under these latter are tubes of iron plate, about 5 feet long, forming continuations of the clay retorts, and upon these iron pipes the clay ones rest. The iron pipes serve for the cooling of the nickel cubes formed in the retort, and they themselves rest, with three-quarters of their periphery, on an iron plate. At the beginning of the operation the retorts are filled to a certain height with small coal, upon which the cubes of oxide of nickel are charged. From time to time part of the contents of the coolers are removed through an opening in the lower part of the tubes. In this way the grains slide down the heated clay retorts, and finally are delivered into the coolers in the metallic condition. The removal of the cubes takes place every three-quarters of an hour or hour. At Val Benoit, in 24 hours, 10 or 12 cwt. of nickel are produced in a furnace with 6 retorts, with a consumption of 18 to 20 cwt. of coal.

Very recently, according to Knut Styffe,[3] furnaces with muffles have been brought into use for preparing spongy nickel. A furnace of this kind holds 12 muffles, which are placed in two rows one above the other, and fired by a single fireplace. The furnace has working doors for each of these rows on opposite sides. The reduction lasts 4 hours. The temperature is raised to 1200°, in consequence of which the reduced nickel sinters into sufficiently solid pieces.

Levat[4] communicates an arrangement of a furnace with a single muffle, illustrated in Fig 320. The furnace is 11½ feet long and 6 feet wide. The muffle has an opening on the short side, and is there closed during the operation by doors (*k k*). These doors are counterpoised and protected within by fireproof linings. Gas fuel is used; *l*, *l*, are the flues through which the flames play round the muffle. The oxide to be reduced is charged into iron vessels *m*, *m*, which are introduced at the side of the furnace opposite the generator, and gradually pushed forward until they are drawn out at the hottest place. Each crucible remains 24 hours in the furnace.

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[1] Kerl, *Metallhüttenkunde*, p. 558.

[2] *Ante*, p. 441.

[3] Oesterr. *Zeitsch*,. 1894, p. 324.

[4] *Loc. cit.*

This furnace serves for the reduction of the mixed nickel and copper oxides, as well as for nickel oxide alone. If the nickel reduced alone is to sinter properly, it must be heated in the crucibles to a temperature of 1100°–1200° for at the very least 4 hours.

The production of molten nickel from the monoxide is carried out, for example, at the Orford Copper Company's works, Bergen Point, New York Harbour.

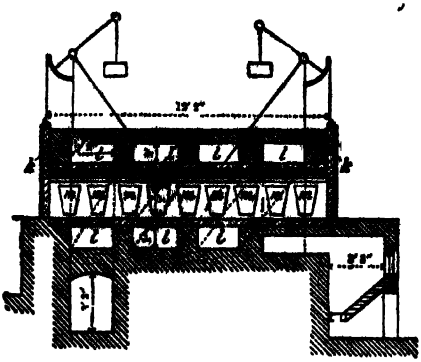

FIG. 320.

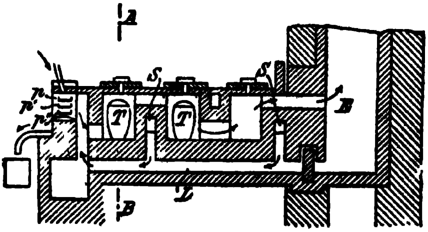

FIG. 321.

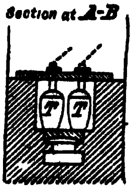

FIG. 322.

According to v. Ehrenwerth,[1] there are used for reduction and fusion, at this place, graphite crucibles 18 inches high and 14 inches wide, in each of which 75 lbs. of nickel monoxide are placed. Wood charcoal is the reducing agent (16 per cent. by weight of the oxide); petroleum fuel is used. The plan of the furnace is shown in Figs. 321, 322. The furnace has 3 chambers each holding 2 crucibles, the furthest chamber always standing empty. The middle chamber gives the crucibles a preliminary heating, and the one nearest the fire serves to melt the reduced nickel. The petroleum flame passes through the various chambers in the direction indicated by the arrows, and finally reaches the chimney E. The petroleum runs first into the uppermost of 3 trays *p*, stretching the full width of the furnace, placed one under another. When the top one is full, the petroleum flows into the next below *p′*, and when that is full into the third *p″*. The petroleum that flows away from the lowest passes into a receiver outside the furnace. The air for the combustion enters through the channels *S*, and then passes in the direction indicated by the arrow, through a channel going under the furnace, for preliminary heating before entering the fireplace. Such a furnace can smelt 3 charges in 12 hours, and produces in this time 2400 lbs. nickel with an expenditure of 105 gallons of petroleum. The liquid nickel is poured into iron moulds and takes the form of bars. The material reduced is said to contain 90 per cent. nickel monoxide, and the metal produced 96 to 98 per cent. nickel and 0·5 per cent. iron.

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[1] *Loc. cit.*, p. 550.

2. EXTRACTION OF NICKEL FROM THE SILICATE (GARNIERITE)

This New Caledonian ore is a silicate of variable composition containing water, the constituents lying between the following limits:—

NiO	9 to 17 per cent.
SiO_2	41 to 46 ,,
Fe_2O_3	5 to 14 ,,
Al_2O_3	1 to 7 ,,
MgO	6 to 9 ,,
H_2O	8 to 16 ,,

The nickel content of the garnierite which is smelted has of late decreased to between 7 and 8 per cent. At present it is treated only in Europe (Glasgow, Birmingham, Havre, Iserlohn). An earlier method of treatment was carried on in the neighbourhood of Noumea in New Caledonia, and consisted in smelting the ore in a blast furnace with coke and fluxes, producing a nickel-iron alloy, which was sent to Europe to be converted into pure nickel.

At Noumea the pulverised ore was mixed with fluorspar, cryolite, soda, manganese ores and powdered coal, and made into bricks with tar. It was then smelted with coke in a furnace 26 feet high, with a blast heated to 400° and at a pressure of 5 inches of mercury; the product was iron-nickel alloy. Limestone was added to combine with the sulphur in the coke, half a ton being needed per ton of ore. If the ore contained too little iron, other ores rich in iron were added. On the average from 1,000 parts of ore 112 parts ferro-nickel were obtained with a consumption of 400 parts coke.

The composition of this ferro-nickel is seen in these analyses:—

	I. Per cent.	II. Per cent.
Carbon	1·70	3·40
Silicon	2·40	0·85
Sulphur	0·55	1·50
Iron	23·30	32·35
Nickel	75·50	60·90

From these it is seen that in spite of the addition of limestone the alloy still contained an appreciable amount of sulphur. The ferro-nickel was exported to Europe, where it was attempted to purify it from sulphur, silicon and iron by oxidising processes. For example, at Septèmes, near Marseilles, the alloy was fused on a hearth of nickel monoxide in a Siemens-Martin furnace, and finally a crude nickel containing manganese was added to remove the oxygen. A lining of chalk to the hearth was used to remove the silicon and sulphur.

This operation attained its aim just as little as any of the other diverse methods, inasmuch as it was not successful in removing iron and sulphur from the nickel. Consequently the production of the nickel-iron alloy has been entirely given up.

At present all the ore raised in New Caledonia is exported. The greater part comes to Europe, and there is smelted into a matte in blast furnaces with the addition of materials containing sulphur. This matte is refined in reverberatory furnaces or converters, or by roasting and smelting in shaft furnaces, and lastly worked up by roasting into nickel oxide, or into nickel by roasting and afterwards reducing. These processes are carried on chiefly in Glasgow, Birmingham, Havre, and at the works of the French "Le Nickel" Co. at Iserlohn.

The ores are smelted in shaft furnaces, which are surrounded with water jackets either throughout their height, or from the bottom to 3 feet 3 inches high. Coke and fluxes containing sulphur are added and the product is a coarse matte. The flux chiefly used is the calcium sulphide, remaining in the manufacture of soda by the Leblanc process; if this cannot be obtained, gypsum is used. By the use of this flux, the whole of the nickel and part of the iron pass into matte. The calcium sulphide is decomposed by the nickel silicate of the garnierite, and nickel sulphide and calcium silicate formed. If gypsum is used it becomes reduced to sulphide in the furnace by the coke, and the action with garnierite then proceeds. The ore is crushed to powder with gypsum and coal, and this mixture pressed into bricks. In 24 hours 25 to 30 tons of ore are put through one of these furnaces. Levat gives the consumption of coke as 30 per cent. of the ore. The matte contains 50—55 per cent. Ni, 25—30 per cent. Fe, and 16—18 per cent. S, and is free from arsenic and copper. Just as above with nickel coarse matte, this can be freed from iron and an equivalent quantity of sulphur in reverberatory furnaces or converters. A refined matte is then obtained with an average composition of 75 per cent. Ni, 24 per cent. S, 0·5 per cent. Fe, and 0·5 per cent. of various impurities. Just like the refined matte from the other ores, this is dead roasted, and reduced to nickel.

The slag obtained from the ore smelting is thrown away. After refining the matte by roasting, and then fusing with sand, this refined product is smelted in the same furnaces with water jackets as are used for the ore. The slag obtained in the refinery contains large quantities of nickel; it is made into bricks after being ground with sand, gypsum and coal, and smelted to a matte in the same furnaces. This matte is subjected to a smelting to concentrate it, and then treated in the same way as the coarse matte obtained from the ore.

3. EXTRACTION OF NICKEL FROM ARSENICAL ORES

The arsenical ores are niccolite or kupfernickel, chloanthite and nickel glance. Only a very small amount of nickel is obtained from these ores, owing to their limited occurrence. Besides gangue, these nickel ores generally contain large quantities of iron, and often sulphur. The metallurgical processes consist of getting rid of the gangue, and separating nickel from iron, arsenic and sulphur. The separation of nickel from iron depends on the fact that the chemical attraction of iron for oxygen is greater than that of nickel, whilst the affinity of arsenic for nickel is greater than its affinity for iron. It is therefore possible to oxidise and slag the iron in the ore, while the nickel is separated as arsenide.

At a sufficiently high temperature nickel arsenide is converted by the oxygen of the air into a mixture of nickel monoxide and arseniate. The latter is mostly converted into monoxide by strongly heating with coal, and afterwards in a current of air. Another way is to remove the arsenic of nickel arsenide as an alkaline arseniate by heating with saltpetre and soda, while the nickel is converted into monoxide. Washing with water removes the alkaline arseniate from this oxide. The nickel monoxide is reduced to nickel as described above.

The production of pure nickel arsenide or nickel speiss from the ores entails roasting and smelting operations. If the ores contain sulphur, or more arsenic than is required to form the compound Ni_2As, they are subjected to an oxidation to remove the sulphur and excess of arsenic; and then reduced in shaft furnaces. But if the ores contain no metallic sulphides and no excess of arsenic but only gangue, they are subjected at once to a smelting, with formation of slag, in shaft furnaces.

Since as a rule there is a large proportion of arsenide of iron in the ores, a speiss is generally obtained which contains iron; it is known as "coarse" speiss, and it rarely consists of only nickel arsenide. It is roasted in order to oxidise it, after which it is smelted in reverberatory or shaft furnaces; it may also be fused and oxidised on a hearth or in a reverberatory furnace, which removes the iron and a corresponding amount of the arsenic. If the speiss is poor in nickel and rich in arsenic and iron, these operations will have to be repeated. The nickel speiss free from iron which is finally obtained —"refined nickel speiss"—is completely roasted in reverberatory furnaces, carbonaceous bodies being mixed with it from time to time to help to remove the arsenic, and at the end of the process saltpetre and soda are added. In this way nickel monoxide is formed, and is reduced in the usual manner.

We must then distinguish three operations:—

a. Conversion of ore into coarse speiss.

b. Conversion of coarse speiss into refined nickel speiss.

c. Conversion of refined nickel speiss into nickel.

a. CONVERSION OF ORE INTO COARSE SPEISS

The basis of this conversion is the following: Ores which contain sulphur, arsenide of iron, or more arsenic than is required to form the compound Ni_2As are calcined and then reduced in shaft furnaces; ores free from sulphur or arsenide of iron, and not containing excess of arsenic, are smelted direct in reverberatory or shaft furnaces with the object of producing a slag.

a. Roasting the Ores

When the ores are free from sulphur, the roasting should be regulated so that the arsenic is brought down to the quantity sufficient to combine with the whole of the nickel to form Ni_4As as the main product of the subsequent smelting. If the roasting is carried too far, and the quantity of arsenic is less than this, nickel will pass into the slag. When sulphur is present, the roasting should remove it as completely as possible, unless there is also copper enough to be worth extracting. In this case sulphur should be retained in such quantity that a copper matte is formed during smelting, and separates from the speiss.

During the roasting arsenic is converted partly into arsenic trioxide, partly into pentoxide. The iron and the nickel arsenides lose arsenic and become converted into oxides. The higher compound of arsenic is formed by the oxidation of the trioxide where it is in contact with red-hot masses of ore, and the red-hot furnace walls; it combines partly with the iron and nickel oxides (with cobalt oxide and with silver also if present). Further, part of this arsenic pentoxide is reduced again to trioxide by contact with undecomposed arsenides, and with the lower metallic oxides, if any should be present. Arseniate of nickel is much more easily produced than the corresponding salt of iron. The arseniates are fairly stable at a high temperature, as they are not readily decomposable by heat alone. If it is desired to remove the arsenic from them, powdered coal or carbonaceous matter is added. By these means iron arseniate is somewhat readily converted into ferric oxide, while the acid radicle is converted into arsenic trioxide and suboxide, with the formation of carbon dioxide. Arseniates of cobalt and nickel are converted into arsenides, which, in a current of air, are converted into oxides and basic arseniates, with a loss of some arsenic as trioxide. The product of the roasting is accordingly a mixture of undecomposed arsenides, oxides and basic arseniates.

If metallic sulphides are present in the ores they are oxidised to sulphates. Vapours of sulphur trioxide are formed from sulphur dioxide by contact action, or from the decomposition of sulphates, and exert an oxidising action on arsenides, which are partly converted into arseniates. Any arsenical pyrites (iron sulphide and arsenide) present in the ore, gives off fumes of sulphide of arsenic; at a red heat it is converted into a mixture of ferric oxide, sulphate and arseniate, setting free sulphur dioxide and arsenic trioxide.

Carbonates of iron and calcium, which are frequently present in nickel ores, are changed into arseniates of those metals, or into a mixture of sulphates and arseniates if sulphides are present. During this heating the heat must not be carried so high that any silica present forms silicate with nickel monoxide, because this nickel silicate is but imperfectly decomposed again, in the subsequent smelting, with the formation of arsenide of nickel. Thus, if sulphides are present in the ore, the product of roasting is a mixture of metallic sulphides, arsenides, oxides, sulphates and arseniates.

The roasting may be performed in heaps, stalls, reverberatory or shaft furnaces, or muffles. Since the complete removal of the arsenic is not really necessary, the ores are roasted in stalls in most works, these stalls allowing of the collection of arsenic trioxide in the chambers attached.

The best forms of apparatus for roasting are reverberatory furnaces and muffles. In the latter it is very easy to attain exactly the desired limit in roasting. If it is necessary to make the fumes quite harmless, or to collect the whole of the arsenic trioxide formed, they should be used.

Stalls were or are in use at Schladming in Styria, Dobschau in Hungary, Leogang in Salzburg.

At Schladming,[1] ores containing 11 per cent. of nickel and 1 per cent. of cobalt were roasted in so-called Bohemian roasting stalls,[2] 16½ feet long, 15 feet wide and 4 feet high, which were connected with condensing chambers for sulphide of arsenic and arsenic trioxide On the brick bottom of the stall was spread 5 inches of wood and a quarter of an inch of wood charcoal, on this 18 or 20 tons of ore spread out to a thickness of about an inch. In the long axes of the stall were two square wooden conduits, to improve the draught, and these were in connection with canals in the floor left free from ore. Before firing the stall a layer of fine ore was placed on the surface of the charge, and then the stall bricked up. Firing was done by shovelling red-hot coals in at the wooden conduits. The roasting lasted 5 to 8 days.

At the George Smelting Works at Dobschau in Hungary, ore containing 4·5 per cent. of nickel and 1·5 per cent. of cobalt was roasted in stalls with arched roofs 10 feet high, 16½ feet long, and 13 feet wide, connected with condensing chambers; 40 tons of ore formed the charge in one stall. The bed was formed of 1¾ – 2 cords wood. The roasting lasted 2 to 3 days.

At the Losonez Works in Hungary,[3] ores containing 14 to 20 per cent. of nickel with cobalt and 0·5 per cent. of copper were roasted in reverberatory furnaces on beds 10 feet square in charges of 16 cwt. to 1 ton. Wood was used as fuel.

A reverberatory gas-furnace designed by Flechner[4] for the roasting of ores and speiss is depicted in Figs. 323, 324, 325. It is said to be used at Schladming, and (with direct firing) in Westphalia. The gas enters the middle of the furnace through the channel *a*, and the air necessary for its combustion is led in through the pipe *f*.

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[1] Badoureau, *Berg. und Hütt. Ztg.*, 1878, p. 205.

[2] *Allg. Hüttenkunde*, p. 328.

[3] *Berg. und Hütt. Ztg.*, 1878, p. 206.

[4] *Ibid.*, 1879, p. 211.

The products of combustion pass through four openings (up-takes) *g*, built in the side walls of the furnace, into the perpendicular channels *b*, and thence into the chimney. The ore is charged into the furnace through two openings *c* in the roof. The working openings are at the four corners of the furnace. In front of each of these is a perpendicular shaft *e* which is connected with the intersecting passages *h*. Waggons are wheeled into the latter in order to remove the roasted products when emptied through the channels *c*.

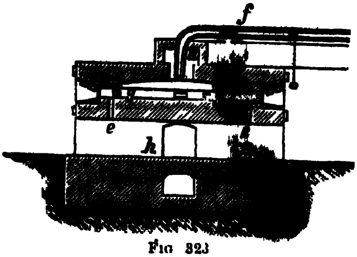

Fig 823

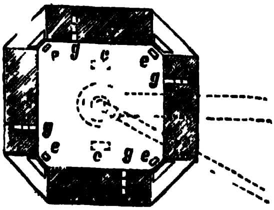

Fig. 824

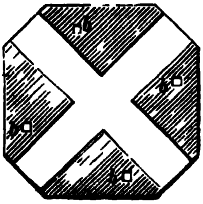

Fig. 825.

β The Smelting of the Nickel Ore into Coarse Speiss

If gangue only has to be separated from the nickel arsenide, the ores are smelted in blast or reverberatory furnaces with the addition of fluxes and slag-forming materials. The slagging away of the gangue is the only chemical change aimed at in this process

But if the ores have been roasted beforehand, and now consist of mixed oxides, arseniates and undecomposed arsenides, with often sulphates and sulphides as well, then the whole amount of nickel in the roasted product has to be collected into a speiss, the gangue to be completely slagged, and the iron as far as is possible. Any copper worth extracting should be collected in a matte. This sort of smelting is usually performed in a blast furnace, but can also be carried out in a reverberatory furnace.

In the blast furnace used as a rule on the continent, ferric oxide is reduced to ferrous and slagged with silica. Nickel monoxide is partly reduced to metal, partly reacts with iron arsenide to form nickel arsenide and ferrous oxide, which latter is also slagged by silica. The metallic nickel takes arsenic from compounds of nickel containing it in larger proportion, and Ni_2As is thus formed, or it takes arsenic from iron arsenide. This latter is thereby reduced to a compound containing less arsenic, or iron is separated if such compounds cannot be formed. The iron may be taken up by the speiss, but part of it reacts with ferric oxide to form ferrous oxide which is slagged.

Nickel arseniate is reduced to arsenide. Iron arseniate loses most of its arsenic in the upper part of the furnace, and arsenic pentoxide is reduced to trioxide by the action of carbon monoxide; this trioxide volatilises, while carbon dioxide is also formed, and ferric oxide is left, which is reduced to ferrous oxide and slagged.

If metallic sulphides, and sulphates of copper and iron are present, the same changes occur as stated above in the smelting of roasted nickel ores containing sulphur. Copper sulphide unites with any metallic sulphides that remain to form a matte. Nickel arsenide unites with any remaining iron arsenide, or other arsenides that may be present, to form a speiss. If the copper present finds no sulphur to combine with, it passes into the speiss. If the matte is in very small quantities it is taken up by both slag and speiss; otherwise it separates out above the speiss.

Earthy matter present, as well as most of the iron, passes into the slag. If there is not enough arsenic present to combine with all the nickel, a corresponding portion is slagged off. Any nickel silicate present, formed by too great heat in the roasting, goes for the most part into the slag. Nickel silicate and iron arsenide do not readily interact, so it is not possible to get back all the slagged nickel into the speiss by such a change.

The smelting is conducted so that a monosilicate containing at least 30 per cent. of ferrous oxide is formed. An acid slag will contain nickel. (According to Badoureau, when nickel and cobalt arsenide are smelted together with a slag containing 30 per cent. of ferrous oxide, the two former metals are practically absent from it.) Otherwise the same principles are observed in the formation of the slag as were laid down above for its formation in smelting the sulphuretted nickel ores in blast furnaces. Further, with regard to the arrangement of the furnaces and conducting of the operation, all that has been said there still applies. The furnaces are constructed usually as crucible furnaces or have fixed fore-hearths.

Kupfernickel containing heavy spar used to be smelted, at Sangerhausen[1] without previous roasting. The blast fu[illegible]e, constructed as a crucible furnace, was 6¼ feet high and 1 foot wide. 1 lb. fluorspar was added as flux to 100 lbs. ore, together with 2 lbs. clay and 4 lbs. quartz, and also a measured quantity of slag from a previous operation. 100 lbs. of ore required 15½ cb. ft. coal. The speiss obtained contained about 40 per cent. of nickel. As instances of the smelting of roasted ore, we may take Schladming in Styria, Dobschau in Hungary, and Leogang in Salzburg.

At Schladming,[2] where the ore was roasted in stalls, and contained 11 per cent. of nickel and 1 per cent. of cobalt, it was smelted in blast furnaces with crucible hearths, 6½ feet high, provided with one tuyere in the back wall. This furnace had a trapezoidal horizontal section, 1½ feet wide in the tuyere wall, 1 foot 9 inches wide in the front wall, and 2 feet deep. The tuyere was 5 feet 7 inches below the mouth, and 10 inches above the bottom. The crucible had two tap holes, each of which communicated with a tapping hearth before the furnace. These hearths were made of slag from ore smelting, worked into a paste with milk of lime. The charge consisted of 89 parts roasted ore, and 19 parts quartz. In 24 hours 5 tons of ore were put through, with the use of 18 cwt. of wood charcoal. The speiss, which was tapped every two hours, contained:—

45	to	47	per cent.	Ni
4	„	6	„ „	Co
8	„	10	„ „	Fe
1	„	1·5	„ „	Cu
33	„	36	„ „	As
1	„	2	„ „	S
1	„	2	„ „	charcoal

At the George Works at Dobschau[3] in 1876, the ore contained 4·5 per cent. of nickel, and 1·5 per cent. of cobalt, and was roasted in stalls. It was then smelted in blast furnaces 16½ feet high, circular in horizontal section, and having two tuyeres. The diameter was 3 feet 4 inches at the level of the tuyere, 4 feet at the mouth. The tuyere was 2¾ inches in diameter, the blast pressure 2½ inches of mercury. The charge was 100 parts ore, 3–4 quartz, 8–12 limestone,

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[1] *Berg. und Hutt. Ztg.*, 1864, p. 59.

[2] *Ibid.*, 1878, p. 205.

[3] *Ibid.*, p. 206.

5–10 rich slag. In 24 hours 7 to 10 tons of ore were put through, with one-fifth the amount of wood-charcoal. The speiss obtained contained from 16 to 20 parts per cent. of nickel and cobalt.

At Leogang, in Salzburg,[1] the calcareous ore containing 2 to 3 per cent. of nickel and cobalt was roasted in stalls, and smelted with the addition of quartz in blast furnaces 4 feet high and 2½ × 2½ feet in plan. The slag obtained contained some cobalt.

The smelting of the ore in reverberatory furnaces seems to be practised only in England. In such the nickel monoxide and arseniate formed in the roasting react with iron arsenide to form ferrous oxide and nickel arsenide. The iron is slagged. Instances of this method have not come to the knowledge of the writer.

b. CONVERSION OF COARSE SPEISS INTO REFINED NICKEL SPEISS

This conversion, which aims at the removal of the iron with its equivalent of arsenic, consists either (1) in roasting the coarse speiss, and then smelting it in blast furnaces, and, if necessary, repeating the whole process on the speiss obtained; or else (2) roasting, smelting in reverberatories, and always repeating the operation on the insufficiently pure product; or else (3) smelting the roasted coarse speiss in crucibles; or else (4) taking the speiss formed by roasting the coarse one and smelting in either of the two sorts of furnaces, then subjecting the product to an oxidising fusion in a reverberatory furnace without previous roasting.

The chemical changes in roasting the speiss are the same as in roasting the ore.

The changes in smelting this roasted speiss in blast furnaces are the same as for similar smelting of roasted ore, except for the slagging of the earthy matter. When the smelting takes place in a reverberatory furnace, the changes are chiefly these; iron arsenide reacts with nickel monoxide and arseniate to form ferrous oxide and nickel arsenide. The ferrous oxide is slagged by means of the silica present in the hearth, or added, or by the addition of potash and soda, while nickel forms a speiss.

Smelting in crucibles entails the same changes as smelting in reverberatory furnaces.

When unroasted speiss undergoes an oxidising fusion in hearths or reverberatories, the iron is first oxidised or converted into iron arseniate (as in the Plattner nickel assay), and then is slagged by means of sand, glass and quartz strewed on the molten metal. After iron follows cobalt, and nickel after that. The process of oxidation can be so regulated by repeated drawing off of slag, and repeated strewing of sand or poor quartzose ores on the molten mass, that nickel remains combined as arsenide, while iron passes into the slag.

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[1] *Berg. und Hütt. Ztg.*, p. 206.

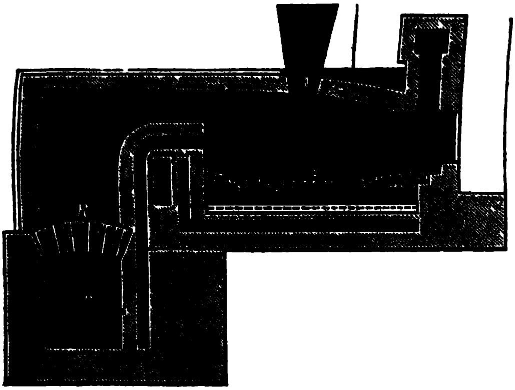

Fig 826

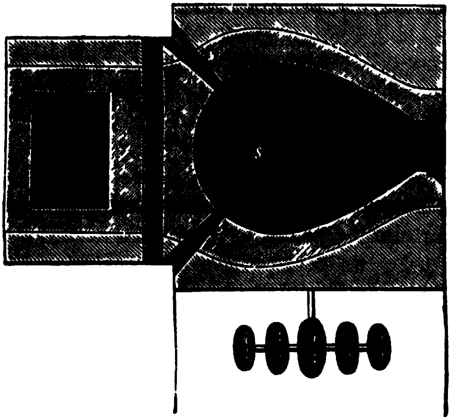

Fig 827.

The roasting of the speiss is carried on in stalls or reverberatory furnaces. Here also condensing chambers are added to make the products harmless, or to collect the arsenic trioxide. The Flechner reverberatory furnace described above[1] has been used, with specially good results, either with gas or with direct firing.

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[1] P. 559.

The blast furnaces for smelting are similar to those used for ore

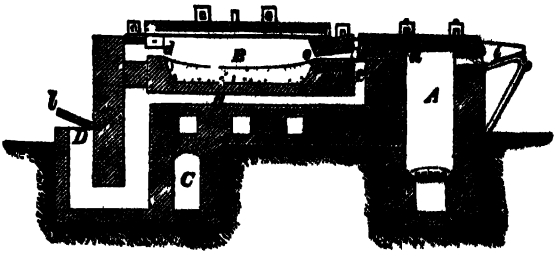

Fig 328

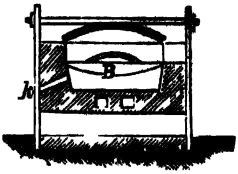

Fig 329

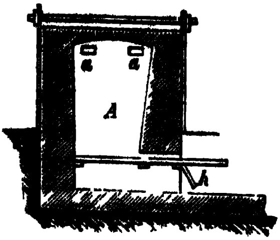

Fig 330

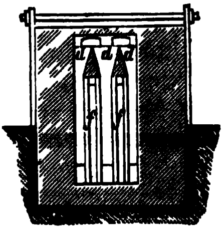

Fig 331

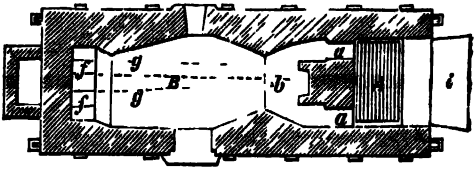

Fig 332

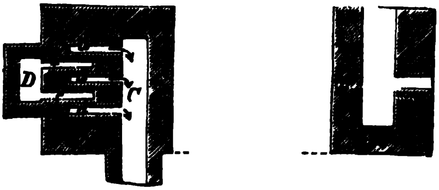

Fig 333

Among reverberatory furnaces for smelting the speiss or for refining it by a blast, the Hungarian furnace and the Flechner one with gas deserve mention.

The arrangement of the Hungarian reverberatory furnace[1] is shown in Figs. 326, 327.

The bed *S* of the furnace, which is 8 feet long and 6½ feet in maximum width, consists of layers one above the other of slag, clay, sand and marl. The smelting hearth is hollowed out in the marl layer. *C* is the roof over the hearth-bed, 2 feet 7 inches high; at the highest point *f* are openings, for the admission of air, 2½ inches wide at the nose. Through these, air at a pressure of 10½ inches of water is blown into the hearth-chamber. The fire-grate is 4 feet 2 inches long and 2½ feet wide. This contains two grates, *R* and *r*, one over the other, of which the upper *R* is made of slag bricks, the lower *r* of iron bars. Wood is burnt on the upper grate; the charred sticks fall through the interstices, shown in the figure, on to the iron grate underneath, where they are completely burned.

The construction of Flechner's reverberatory furnace with gas fuel is shown in Figs. 328 to 333.

A is the gas-producer, *B* the hearth, *C* the flue. The air for the combustion of the gases enters at *D*, and ascends through the channels *f*, which are placed between *d*, *d*, the exit-flues for combustion products. It is warmed in the pipe *g*, passing under the hearth of the furnace, and then passes on through the ports *c* into the chamber *b*, where it is mixed with the gases streaming out from the producer through the channel *a*. The burning gases pass through the port *c* into the heating chamber, and thence through the port *d* into the chimney *C*. Through the hopper *i* the fuel is introduced into the producer. The roof of the furnace is movable on hinges. The air for combustion is regulated by the valve *l*.

At the George Works at Dobschau,[2] coarse speiss containing 16 to 26 per cent. of nickel and cobalt was roasted in stalls with from 3 to 5 firings, and then smelted to a concentrated speiss in blast furnaces similar to those used for the ore.[3] In 24 hours 11 tons of speiss, with 23 per cent. of quartz and 26·5 per cent. of charcoal, were put through. The concentrated speiss contained—

Ni and Co	31·9	per cent.
Cu	1·9	„
Fe	26·4	„
As	36·3	„
S	3·1	„

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[1] *Berg. und Hütt. Ztg.*, 1878, p. 206; Kerl, *Metallhüttenkunde*, p. 538.

[2] *Berg. und Hütt. Ztg.*, 1878, p. 206.

[3] P. 562.

This speiss was roasted three or four times in stalls, and then again smelted to a doubly concentrated speiss in one of the Hungarian furnaces described above. The charge in it was 1·8 to 2 tons of roasted speiss. When the roasted material was all fused, which took 10 hours, the air blast was turned on, and glass, quartz and soda were added. To prevent cobalt in appreciable quantity being slagged, the whole of the iron was not removed, but the blast stopped when the iron, all but 8 or 10 per cent., was removed (after 12 to 14 hours). 100 parts of the roasted concentrated speiss required 2 parts of glass, 4 of quartz, and 1 of soda The doubly concentrated speiss had this composition:—

Ni and Co	50—52	per cent.
Cu	1— 2	"
Fe	8—10	"
As	38—40	"
S	1— 2	"

The slag contained 1 or 2 per cent Ni and Co, and was added to ores during smelting. From the doubly concentrated speiss nickel and cobalt were extracted.

At the Maudling Works[1] in Austria, the coarse speiss from Schladming in Styria was worked up. It contained 45 to 47 per cent. of nickel and 4 to 6 per cent. of cobalt. It was first roasted in a reverberatory furnace with octagonal hearth and eight working doors, the central fireplace being situated under the middle of the bed. After this it was smelted in graphite crucibles with potash and quartz. The crucibles were placed eight in each air furnace, and each contained 35 to 45 lbs. of the roasted coarse speiss, with 30 per cent. potash and 12 per cent. quartz. The heating of this furnace took 3 hours, then the fusion took place after 6 hours more; the crucibles remained 17 more hours in the fire, and then were taken out and emptied. In 24 hours 194 cub. ft. charcoal were used. 100 parts of roasted coarse speiss gave 55 refined speiss with 67 per cent. of Ni, Co and Cu, 2 per cent. of Fe and 31 per cent. of As. The slag was a mixture of arseniates and silicates of cobalt and iron.

At Leogang, in Salzburg,[2] the coarse speiss was roasted in stalls three or four times, and then smelted to a concentrated speiss in blast furnaces with quartz and slag from the first smelting. The latter speiss was subjected to a blast in a Hungarian reverberatory furnace on a quartz bed. The blast was continued with repeated removal of slag and addition of sand until all the iron was slagged. The slag resulting contained cobalt, and was smelted with quartz and arsenic into a cobalt speiss.

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[1] *Berg. und Hütt. Ztg.*, 1878, p. 206. [2] *Ibid.*

c. CONVERSION OF REFINED SPEISS INTO RAW NICKEL

This conversion is effected by a complete roasting of the speiss and subsequent reduction to metal.

a. The Dead Roasting of Refined Nickel Speiss

The object of this is to convert the arsenide of nickel entirely into monoxide. It is done by repeated roasting, the decomposition of any arseniate formed being ensured by the addition of carbonaceous matter, or part of the arsenic may be converted into alkaline arseniate by the addition of saltpetre and soda during the roasting. Again, the two treatments may be combined, and first carbonaceous matter, secondly saltpetre (alone or with soda) added to the speiss during roasting.

Nickel arsenide is oxidised to monoxide and to arseniate, while arsenic trioxide escapes. The arseniate may be made to give off some arsenic and form a basic compound by raising the temperature. But in presence of carbon it is reduced to arsenide, which again becomes converted partly into monoxide, partly into arseniate, by oxidation, while more arsenic trioxide is given off. The amount of arseniate present thus diminishes, and in this way, by alternate oxidation, and reduction, all the arsenic is finally removed.

Again, the addition of saltpetre to the charge converts the arsenic into an alkaline arseniate, easily removed by washing with water. By taking advantage of this action the last portions of arsenic and of sulphur are removed, the sulphur as alkaline sulphate. Frequently soda, or soda and salt, is added with the saltpetre. By the action of the salt some arsenic chloride (and antimony chloride from any antimony present) are formed and volatilised.

(Apart from roasting, arsenic may be removed also by smelting the speiss with saltpetre and soda, or smelting it with soda and sulphur, and washing out the salts formed; or it can be removed in the form of sulphide of arsenic by heating the speiss with sulphur in absence of air.)

At Schladming[1] the refined speiss was completely roasted in a furnace, of which the construction may be seen in Figs. 334, 335, 336.[2]

The fireplace *f* lay under the hearth *H*, which was 6 feet 6 inches square. The gaseous products of combustion passed up the perpendicular chimney *k* opening into the heating chamber in the middle of the hearth. They left this latter by four openings *z* at the four corners, which openings served also as working ports, thence into chimney hoods over the corners, and over the arch of the furnace into the chimney *y*.

The charge in the furnace was 4 cwt of speiss, which was dead roasted in 24 hours, using wood fuel After 20 hours had elapsed, about 45 lbs. of a mixture of equal quantities of saltpetre and soda was added, which converted the arsenic still present into alkaline arseniate. This was dissolved out after the roasting, in a tub with water. The residue consisted of nickel oxide.

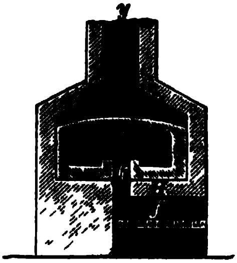

FIG. 334

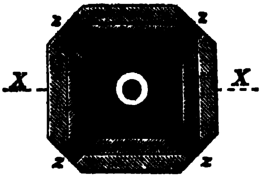

FIG. 335.

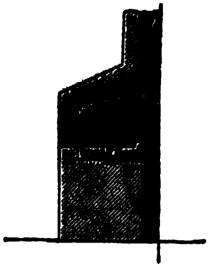

FIG. 336

At the George Works at Dobschau, in Hungary, the refined speiss was roasted, in 1867, in a reverberatory with double hearth. Towards the end of the first roasting, pine needles or charcoal dust was added to the mass at intervals of about half an hour. The product was sieved and ground, and then mixed with 10 per cent. of its weight of soda, 5 per cent. of saltpetre, and 10 per cent. of sea salt, and subjected to a second roasting for 4 hours. In this, arsenic and antimony were partly volatilised as chlorides, partly converted into alkaline arseniates and antimoniates. On account of these the mass remained pasty for 2 hours. After the roasting the arseniates and antimoniates were removed by repeated washing with hot water.

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[1] *Berg. und Hütt. Ztg.*, 1878, p. 228.

[2] Kerl, *Metallhüttenkunde*, p. 548.

β. Reduction of Dead Roasted Speiss to Crude Nickel

This is done in the same way as the reduction of a completely roasted matte of nickel, given above.[1] If the speiss contains copper, so will the crude nickel. At Schladming in Styria, from 1860 to 1867,[2] the dead roasted and ground speiss was mixed with 4 per cent. of syrup, and made up on a tin plate into cakes weighing 3·7 lbs., 6 inches wide, 10 inches long, and $\frac{1}{8}$ inch thick; these were dried and cut into cubes. The cubes were dried in the sun or in a baking-oven and reduced to metal in crucibles of fire-clay. Each crucible took a charge of 26 to 29 lbs. of the cubes of nickel monoxide, with 3 lbs. of coal dust; 40 crucibles were placed in a round furnace, represented in Figs. 337, 338. *R* is the heating chamber which receives the crucibles; the fireplace is below it. The products of combustion pass from the fireplace *r* through an opening *o* in the middle of the bed into the heating chamber, thence through 6 flues *z* into a chamber above the arch of the furnace, thence into the chimney *c*.

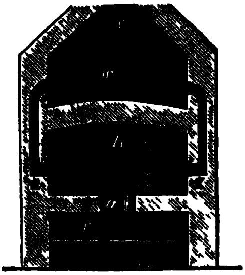

Fig. 337.

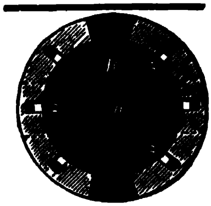

Fig. 338.

The heating of the crucibles, performed with wood fuel, lasted 48 hours. At each operation 7 cwt. of crude nickel were obtained.

B EXTRACTION OF NICKEL FROM METALLURGICAL PRODUCTS

Nickel or its alloys can be extracted in the dry way from various metallurgical residues, particularly certain forms of speiss obtained from copper, lead and silver ores which contain nickel as an impurity, often very slight in quantity. Further, coarse or blister-copper frequently contains nickel, which collects in this product if there is but little arsenic in the copper ore; and there are also slags and iron sows containing nickel.

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[1] P. 551.

Berg. und Hutt. Ztg. 1878, p. 244.

The speiss is worked up in the same way as the coarse speiss obtained in the extraction of nickel from its arsenical ores. If it contains large quantities of lead, copper and silver, it is sought to separate lead and silver as an alloy (argentiferous lead) and the copper as a matte. Lead may always be removed from the speiss by roasting and reduction, and takes with it the greater part of any silver that may be present. Thus most of the silver is disposed of in the same process. The copper is converted into sulphide by smelting with heavy spar, or with pyrites if that cannot be obtained. There results after these operations a speiss richer in nickel and mostly free from the other metals, and this is worked up by the processes mentioned above.

So, for example, at Freiberg, a speiss containing all three of the above metals served for the extraction of the three, and was smelted several times in a blast furnace with the addition of heavy spar, lead residues and slag, and was converted into argentiferous lead, copper matte, and a speiss containing but little silver, lead and copper. The speiss thus enriched in cobalt and nickel up to 15 or 18 per cent. was smelted in a reverberatory furnace without any previous roasting, with the addition of 50 to 60 per cent. of heavy spar, and 20 to 25 per cent. of quartz; the products were a copper matte containing lead, and a speiss containing 40 to 44 per cent. of nickel, 8 per cent. of copper, and free from iron.

Copper containing nickel is subjected to a blast, which gives a dross containing nickel, and copper free from it. The dross may be smelted in a blast furnace again to coarse copper containing nickel, or it may be smelted into a speiss when large quantities of arsenic and antimony are present. This coarse copper from the dross, called dross or waste copper, gives on refining or subjecting to the blast a second dross richer in nickel and cobalt. By smelting this in a furnace, copper still richer in nickel is obtained. So by the repetition of these processes the final result is a nickel-copper alloy, which is sold to the nickel works.

Or again, the dross may be smelted with pyrites to a matte containing nickel, or with heavy spar and arsenical pyrites to a speiss and a copper matte. Again, nickel can be extracted from coarse copper in the wet way.

The metal is obtained from slags containing nickel without copper by smelting them in blast furnaces with heavy spar or pyrites, yielding a nickel-bearing matte, or with arsenical pyrites, giving a nickel speiss. But if the slag holds copper in quantities worth recovering, the smelting is carried on with arsenical pyrites and either heavy spar or iron pyrites, so as to obtain nickel in a speiss, copper for the most part in a matte. This does not effect a satisfactory separation. It is therefore necessary, in case the separation is very incomplete, to treat again the speiss containing copper and the matte containing nickel with heavy spar and arsenical pyrites.

For example, in Altenau the slags from the refining of dross copper, containing both copper and nickel, were smelted in blast furnaces with iron pyrites and arsenical pyrites to a speiss and a matte of the following compositions:—

	Speiss.	Matte.
Ni and Co.	26·77	6·10
Cu	19·85	37·24
Fe	15·82	20·84
Pb	12·14	16·10
As	12·15	trace
Sb	10·01	0·47
S	4·57	19·25

The speiss was roasted in heaps three times over, and then re-smelted in the same way, with 5 per cent. arsenical pyrites, 12·5 per cent. heavy spar, 50 per cent. slag from copper refining, and 50 per cent. slags from lead matting, into a second speiss and matte. Of these the compositions are:—

	Speiss.	Matte.
Ni	35·13	4·37
Cu	17·18	37·45
Fe	8·41	12·68
Pb	6·59	22·81
As	18·65	trace
Sb	10·82	trace
S	2·16	24·48
Co	10·70	—

The speiss was disposed of to cobalt works.

When nickel is to be extracted from iron sows, they may be subjected to a blast in small refining hearths, and the iron oxide resulting slagged with quartz. In this way alloys are ultimately produced containing much nickel and copper; the method was formerly in use at Klefva, in Sweden. Or by using the blast on a small hearth, and strewing nickel, coarse matte or nickel ore on the mass, the nickel will be obtained in a matte. This was practised formerly at the Ringerick Works, in Norway.

At one works in Saxony,[1] iron sows are treated, which contain molybdenum, the composition being 80 per cent. of Fe, 2·5 per cent. of Cu, 2 per cent. of Ni, 1·5 per cent. of Co, 6 per cent. of Mo, 8 per cent. of S. After being broken small they are roasted in a reverberatory furnace and then subjected to oxidising smelting in a similar furnace with quartz as a slagging material; in this way the greater part of the iron is slagged off, and a regulus is obtained, rich in molybdenum, nickel and cobalt. This latter is heated to redness in a reverberatory with saltpetre and soda, so as to form alkaline molybdates. These are removed by lixiviation, and the residue consists chiefly of a mixture of oxides of nickel, cobalt and copper. This is smelted into a speiss with arsenical pyrites.

C. New Proposals for the Extraction of Nickel from its Ores, and from Metallurgical Products, in the Dry Way

Among new dry methods that have been suggested, Mond's requires mention. In this the nickel in ores or residues, in which it occurs as monoxide, is removed as nickel carbonyl [$Ni(CO)_4$], which is decomposed into nickel and carbon monoxide at a higher temperature. Mond discovered that finely divided nickel in the presence of carbon monoxide at a temperature below 150° was converted into gaseous nickel carbonyl. This compound condensed to a colourless liquid, boiling at 43°, and the vapour was decomposed into its constituents on heating to 180°.

According to Mond, nickel monoxide should first be produced by roasting the ores or residues (especially the Canadian pyrrhotite), and this compound reduced to nickel by means of hydrogen, or some other gaseous reducing agent, at a temperature of 350° to 400°. The metal obtained by this method in a state of very fine division should be exposed to a current of carbon monoxide at a temperature of 50°, when the nickel volatilises in the form of nickel carbonyl. The current of gas containing this compound is to be led into closed vessels, in which, when they are heated to 180°, nickel is deposited in the metallic form and exceedingly pure. The carbon monoxide set free can be used again in the process.

This operation, which would seem to be surrounded by many technical difficulties, has been carried out on the large scale in Birmingham. There is no account to hand of the economic results obtained.

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[1] *Berg. und Hütt. Ztg.*, 1878, p. 213.

II. EXTRACTION OF NICKEL IN THE WET WAY

The wet way is especially used at present to extract pure nickel or nickel oxide from speiss and matte containing copper and cobalt. *It is most unusual to submit ores directly to such a process, for in* the great majority of cases it is cheaper to concentrate the nickel first in the dry way, forming a speiss or matte. This is especially true of ores containing sulphur and arsenic. A great variety of methods have recently been proposed for extracting nickel in the wet way from the ores in which it occurs as silicate (garnierite), though very few of these seem ever to have been applied. At present it still seems more profitable with these ores to concentrate the amount of nickel, even although not very high, and to form a matte in the dry way.

We distinguish then:—

A. Extraction of nickel directly from the ores.
B. „ „ from smelting products.

A. EXTRACTION OF NICKEL DIRECT FROM THE ORES

If the ores contain arsenic or sulphur they must be roasted before being treated with solvents. (Sulphuretted ores may be prepared for a wet method by smelting with potassium carbonate and sulphur, as at the Gap Mine, Pennsylvania.)[1] Ores such as garnierite, containing nickel silicate, can be treated direct with solvents. Hydrochloric acid is generally the one used, occasionally dilute sulphuric acid. The latter, however, causes the formation of a precipitate of calcium sulphate afterwards, during the treatment of the solution with carbonate of lime and milk of lime.

Ferric sulphate has been suggested by Emmens[2] (Gossan process) as the solvent for the sulphuretted ores of Canada. According to him the nickel in Canadian pyrrhotite is dissolved out by this reagent, even from the unroasted ore, but the solution of nickel from the roasted ore seems to be very much more rapid. Emmens therefore suggests the roasting of the ore in furnaces, or the weathering of it, and subsequently treating it with ferric sulphate in wooden vats. Nickel is to be precipitated from the liquor as hydrate. The process has not yet been put into practice.

This process has been tried experimentally by the Canadian Copper Company, but not brought into definite use. In the most favourable cases only one-third of the amount of nickel and two-thirds of the copper of the ore are brought into solution by ferric sulphate.[1]

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[1] *Berg. und Hütt. Ztg.*, 1877, p. 300.

[2] *Mineral Industry*, 1892, p. 355.

Macfarlane proposed to convert the nickel of the Canadian sulphuretted ore into chloride by roasting with common salt, and to leach the product with water to dissolve this chloride. Iron was to be precipitated from the liquor by a small quantity of caustic soda, and any copper present by sodium sulphide. Finally the nickel was to be precipitated as hydrate by caustic soda. But nothing is as yet known with regard to the extent to which this method is put into practice.

Ricketts[2] brings nickel and copper into solution as sulphates, and then precipitates the nickel as basic sulphate by alkalies and alkaline sulphates. The basic sulphate is converted into monoxide by strong heating. Then the copper remaining in solution can be deposited electrolytically.

Richardson[3] converts both nickel and copper into chlorides, and separates the two salts by fractional distillation in an atmosphere of hydrochloric acid gas.

The way in which the solution is generally treated is as follows.—

It is first treated with sulphuretted hydrogen or an alkaline sulphide to precipitate copper, bismuth, lead, arsenic and any metals precipitable by these reagents. Then it is treated with chloride of lime to convert the iron into peroxide, which is precipitated by calcium carbonate. With the iron any arsenic present is got rid of as iron arseniate. Next comes the separation of cobalt as sesquioxide by chloride of lime. Finally the nickel is precipitated as nickelous hydrate by milk of lime or soda. The hydrate is converted into oxide by heating to redness, ground up fine, and treated with dilute acid to remove excess of chalk and calcium sulphate.

If copper is to remain with nickel, and an alloy of the two finally produced, the liquid can be treated at once with calcium carbonate, after previously oxidising the iron, and thus removing arsenic and iron. This is as long as the metals of the sulphuretted hydrogen group, other than arsenic, are absent

Occasionally the nature of the ore renders modifications of these processes necessary. Further, special plans have very recently been elaborated for the treatment of nickel silicate, garnierite in particular, but have come to a very small extent into practical use, and therefore can only be mentioned shortly.

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[1] *Mineral Industry*, 1894, p. 463.

[2] American Patents of Oct. 3, 1893, and Feb. 6, 1894.

[3] American Patent, April 10, 1894.

Formerly arsenical ores of nickel were worked by the wet method in Hungary[1] and in Bohemia; it is now no longer used for these ores. The ores were treated with hydrochloric acid after preliminary roasting (Louyet's process), and the solution was diluted with water, to precipitate the bismuth as basic chloride. Then chloride of lime was added, to oxidise ferrous oxide and arsenious oxide, after which milk of lime precipitated ferric hydrate and arseniate. Copper was precipitated by sulphuretted hydrogen or sulphide of barium, then cobalt as sesquioxide with chloride of lime, and lastly nickelous hydrate by milk of lime.

At Joachimsthal[2] in Bohemia the silver ores containing from 5 to 10 per cent. of nickel and cobalt were formerly roasted in a current of steam. Silver was then separated as metal and nickel, and cobalt arseniates were formed. The roasted product was first treated with dilute sulphuric acid, and then with hot nitric acid. The former dissolved nickel and cobalt arseniates, the latter the silver and the remaining cobalt and nickel. After the silver had been precipitated by common salt the nitric acid solution was mixed with the sulphuric acid solution, and the whole treated with ferric chloride to convert the arsenic into ferric arseniate. Powdered limestone caused the precipitation of ferric arseniate, and from the solution remaining cobalt and nickel were successively thrown down by chloride of lime and milk of lime respectively.

Special proposals to separate nickel from silicates (garnierite and rewdanskite) are as follows:—

Herman[3] heats rewdanskite with sulphuric acid in stoneware vessels until the acid begins to vaporise, lixiviates the mass, oxidises the iron with salt and saltpetre, precipitates it by chalk, and precipitates nickel sulphide by sodium sulphide. This is completely roasted and the monoxide reduced.

Laroche[4] treats garnierite with its own weight of sulphuric acid 56° to 60° B., washes the solid product with warm water, and adds ammonium sulphate in quantity equivalent to the nickel sulphate present, and thus separates crystals of nickel-ammonium sulphate from the solution by evaporating down and cooling. These are dissolved in boiling water, and nickel carbonate precipitated by solution of soda. Instead of ammonium sulphate, an equivalent quantity of alkaline oxalate may be added, and nickel oxalate thrown smelting is usually performed in a blast furnace, but can also be carried out in a reverberatory furnace.

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[1] *Berg. und Hütten. Ztg.*, 1849, p. 800.

[2] Kerl, *Metallhüttenkunde*, p. 554.

[3] *Berg. und Hütt. Ztg.*, 1876, p. 308.

[4] Wagner, *Jahresberichte*, 1879, p. 235.

In the blast furnace used as a rule on the continent, ferric oxide is reduced to ferrous and slagged with silica. Nickel monoxide is partly reduced to metal, partly reacts with iron arsenide to form nickel arsenide and ferrous oxide, which latter is also slagged by silica. The metallic nickel takes arsenic from compounds of nickel containing it in larger proportion, and Ni_2As is thus formed, or it takes arsenic from iron arsenide. This latter is thereby reduced to a compound containing less arsenic, or iron is separated if such compounds cannot be formed. The iron may be taken up by the speiss, but part of it reacts with ferric oxide to form ferrous oxide which is slagged.

Nickel arseniate is reduced to arsenide. Iron arseniate loses most of its arsenic in the upper part of the furnace, and arsenic pentoxide is reduced to trioxide by the action of carbon monoxide; this trioxide volatilises, while carbon dioxide is also formed, and ferric oxide is left, which is reduced to ferrous oxide and slagged.

If metallic sulphides, and sulphates of copper and iron are present, the same changes occur as stated above in the smelting of roasted nickel ores containing sulphur. Copper sulphide unites with any metallic sulphides that remain to form a matte. Nickel arsenide unites with any remaining iron arsenide, or other arsenides that may be present, to form a speiss. If the copper present finds no sulphur to combine with, it passes into the speiss. If the matte is in very small quantities it is taken up by both slag and speiss; otherwise it separates out above the speiss.

Earthy matter present, as well as most of the iron, passes into the slag. If there is not enough arsenic present to combine with all the nickel, a corresponding portion is slagged off. Any nickel silicate present, formed by too great heat in the roasting, goes for the most part into the slag. Nickel silicate and iron arsenide do not readily interact, so it is not possible to get back all the slagged nickel into the speiss by such a change.

The smelting is conducted so that a monosilicate containing at least 30 per cent. of ferrous oxide is formed. An acid slag will contain nickel. (According to Badoureau, when nickel and cobalt arsenide are smelted together with a slag containing 30 per cent. of ferrous oxide, the two former metals are practically absent from it.) Otherwise the same principles are observed in the formation of the slag as were laid down above for its formation in smelting the sulphuretted nickel ores in blast furnaces. Further, with regard to the arrangement of the furnaces and conducting of the operation, all that has been said there still applies. The furnaces are constructed usually as crucible furnaces or have fixed fore-hearths.

Kupfernickel containing heavy spar used to be smelted at Sangerhausen[1] without previous roasting. The blast furnace, constructed as a crucible furnace, was 6¼ feet high and 1 foot wide. 1 lb. fluorspar was added as flux to 100 lbs. ore, together with 2 lbs. clay and 4 lbs. quartz, and also a measured quantity of slag from a previous operation. 100 lbs. of ore required 15½ cb. ft. coal. The speiss obtained contained about 40 per cent of nickel. As instances of the smelting of roasted ore, we may take Schladming in Styria, Dobschau in Hungary, and Leogang in Salzburg.

At Schladming,[2] where the ore was roasted in stalls, and contained 11 per cent. of nickel and 1 per cent. of cobalt, it was smelted in blast furnaces with crucible hearths, 6½ feet high, provided with one tuyere in the back wall. This furnace had a trapezoidal horizontal section, 1½ feet wide in the tuyere wall, 1 foot 9 inches wide in the front wall, and 2 feet deep. The tuyere was 5 feet 7 inches below the mouth, and 10 inches above the bottom. The crucible had two tap holes, each of which communicated with a tapping hearth before the furnace. These hearths were made of slag from ore smelting, worked into a paste with milk of lime. The charge consisted of 89 parts roasted ore, and 19 parts quartz. In 24 hours 5 tons of ore were put through, with the use of 18 cwt. of wood charcoal. The speiss, which was tapped every two hours, contained:—

45	to	47	per	cent.	Ni
4	„	6	„	„	Co
8	„	10	„	„	Fe
1	„	1·5	„	„	Cu
33	„	36	„	„	As
1	„	2	„	„	S
1	„	2	„	„	charcoal

At the George Works at Dobschau[3] in 1876, the ore contained 4·5 per cent. of nickel, and 1·5 per cent. of cobalt, and was roasted in stalls. It was then smelted in blast furnaces 16½ feet high, circular in horizontal section, and having two tuyeres. The diameter was 3 feet 4 inches at the level of the tuyere, 4 feet at the mouth. The tuyere was 2¾ inches in diameter, the blast pressure 2½ inches of mercury. The charge was 100 parts ore, 3–4 quartz, 8–12 limestone,

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[1] *Berg. und Hütt. Ztg.*, 1864, p. 59.

[2] *Ibid.*, 1878, p. 205.

[3] *Ibid.*, p. 206.

5–10 rich slag. In 24 hours 7 to 10 tons of ore were put through, with one-fifth the amount of wood-charcoal. The speiss obtained contained from 16 to 20 parts per cent. of nickel and cobalt.

At Leogang, in Salzburg,[1] the calcareous ore containing 2 to 3 per cent. of nickel and cobalt was roasted in stalls, and smelted with the addition of quartz in blast furnaces 4 feet high and 2½ × 2½ feet in plan. The slag obtained contained some cobalt.

The smelting of the ore in reverberatory furnaces seems to be practised only in England. In such the nickel monoxide and arseniate formed in the roasting react with iron arsenide to form ferrous oxide and nickel arsenide. The iron is slagged. Instances of this method have not come to the knowledge of the writer.

b. CONVERSION OF COARSE SPEISS INTO REFINED NICKEL SPEISS

This conversion, which aims at the removal of the iron with its equivalent of arsenic, consists either (1) in roasting the coarse speiss, and then smelting it in blast furnaces, and, if necessary, repeating the whole process on the speiss obtained; or else (2) roasting, smelting in reverberatories, and always repeating the operation on the insufficiently pure product; or else (3) smelting the roasted coarse speiss in crucibles; or else (4) taking the speiss formed by roasting the coarse one and smelting in either of the two sorts of furnaces, then subjecting the product to an oxidising fusion in a reverberatory furnace without previous roasting.

The chemical changes in roasting the speiss are the same as in roasting the ore.

The changes in smelting this roasted speiss in blast furnaces are the same as for similar smelting of roasted ore, except for the slagging of the earthy matter. When the smelting takes place in a reverberatory furnace, the changes are chiefly these; iron arsenide reacts with nickel monoxide and arseniate to form ferrous oxide and nickel arsenide. The ferrous oxide is slagged by means of the silica present in the hearth, or added, or by the addition of potash and soda, while nickel forms a speiss.

Smelting in crucibles entails the same changes as smelting in reverberatory furnaces.

When unroasted speiss undergoes an oxidising fusion in hearths or reverberatories, the iron is first oxidised or converted into iron arseniate (as in the Plattner nickel assay), and then is slagged by means of sand, glass and quartz strewed on the molten metal. After iron follows cobalt, and nickel after that. The process of oxidation can be so regulated by repeated drawing off of slag, and repeated strewing of sand or poor quartzose ores on the molten mass, that nickel remains combined as arsenide, while iron passes into the slag.

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[1] *Berg. und Hütt. Ztg.*, p. 206.

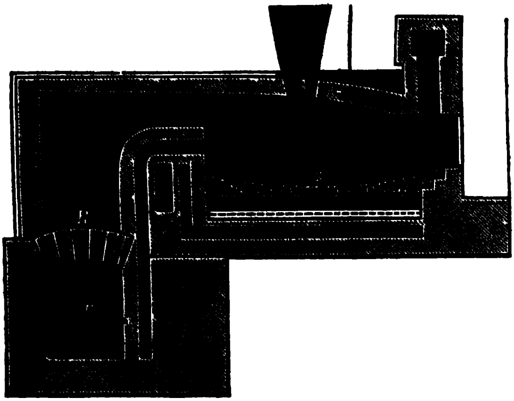
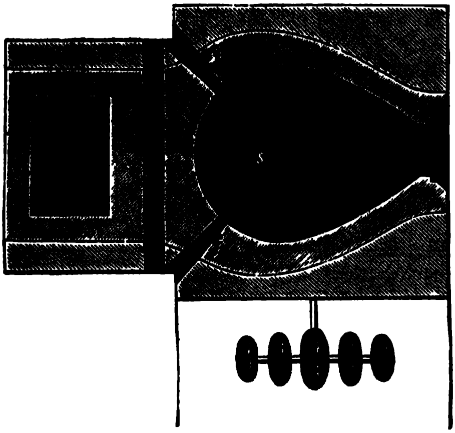


FIG 326



The roasting of the speiss is carried on in stalls or reverberatory furnaces. Here also condensing chambers are added to make the products harmless, or to collect the arsenic trioxide. The Flechner reverberatory furnace described above[1] has been used, with specially good results, either with gas or with direct firing.

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[1] P. 559.

The blast furnaces for smelting are similar to those used for ore.

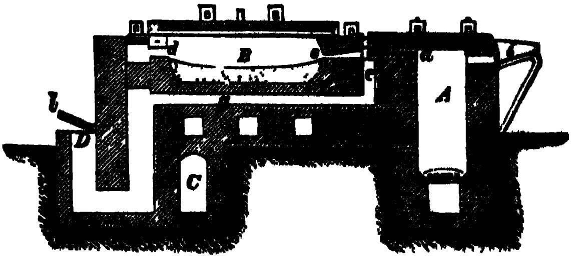

Fig. 328

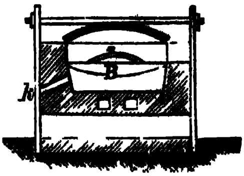

Fig. 329.

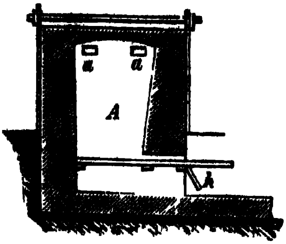

Fig. 330

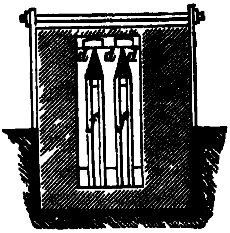

Fig. 331

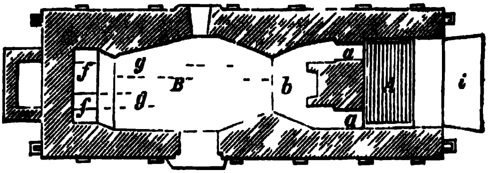

Fig. 332

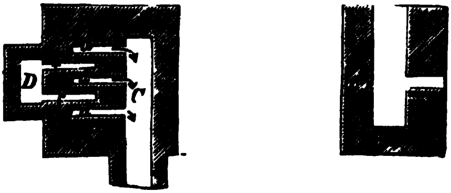

Fig. 333

Among reverberatory furnaces for smelting the speiss or for refining it by a blast, the Hungarian furnace and the Flechner one with gas deserve mention.

The arrangement of the Hungarian reverberatory furnace [1] is shown in Figs. 326, 327.

The bed *S* of the furnace, which is 8 feet long and 6½ feet in maximum width, consists of layers one above the other of slag, clay, sand and marl. The smelting hearth is hollowed out in the marl layer. *C* is the roof over the hearth-bed, 2 feet 7 inches high; at the highest point *f* are openings, for the admission of air, 2½ inches wide at the nose. Through these, air at a pressure of 10½ inches of water is blown into the hearth-chamber. The fire-grate is 4 feet 2 inches long and 2½ feet wide. This contains two grates, *R* and *r*, one over the other, of which the upper *R* is made of slag bricks, the lower *r* of iron bars. Wood is burnt on the upper grate; the charred sticks fall through the interstices, shown in the figure, on to the iron grate underneath, where they are completely burned.

The construction of Flechner's reverberatory furnace with gas fuel is shown in Figs. 328 to 333.

A is the gas-producer, *B* the hearth, *C* the flue. The air for the combustion of the gases enters at *D*, and ascends through the channels *f*, which are placed between *d*, *d*, the exit-flues for combustion products. It is warmed in the pipe *g*, passing under the hearth of the furnace, and then passes on through the ports *c* into the chamber *b*, where it is mixed with the gases streaming out from the producer through the channel *a*. The burning gases pass through the port *e* into the heating chamber, and thence through the port *d* into the chimney *C*. Through the hopper *i* the fuel is introduced into the producer. The roof of the furnace is movable on hinges. The air for combustion is regulated by the valve *l*.

At the George Works at Dobschau,[2] coarse speiss containing 16 to 26 per cent. of nickel and cobalt was roasted in stalls with from 3 to 5 firings, and then smelted to a concentrated speiss in blast furnaces similar to those used for the ore.[3] In 24 hours 11 tons of speiss, with 23 per cent. of quartz and 26·5 per cent. of charcoal, were put through. The concentrated speiss contained—

Ni and Co	31·9 per cent.
Cu	1·9 „
Fe	26·4 „
As	36·3 „
S	3·1 „

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[1] *Berg. und Hütt. Ztg.*, 1878, p. 206; Kerl, *Metallhüttenkunde*, p. 538.

[2] *Berg. und Hütt. Ztg.*, 1878, p. 206.

[3] P. 562.

This speiss was roasted three or four times in stalls, and then again smelted to a doubly concentrated speiss in one of the Hungarian furnaces described above. The charge in it was 1·8 to 2 tons of roasted speiss. When the roasted material was all fused, which took 10 hours, the air blast was turned on, and glass, quartz and soda were added. To prevent cobalt in appreciable quantity being slagged, the whole of the iron was not removed, but the blast stopped when the iron, all but 8 or 10 per cent., was removed (after 12 to 14 hours). 100 parts of the roasted concentrated speiss required 2 parts of glass, 4 of quartz, and 1 of soda. The doubly concentrated speiss had this composition:—

Ni and Co	50—52	per cent.
Cu	1— 2	„
Fe	8—10	„
As	38—40	„
S	1— 2	„

The slag contained 1 or 2 per cent Ni and Co, and was added to ores during smelting. From the doubly concentrated speiss nickel and cobalt were extracted.

At the Maudling Works[1] in Austria, the coarse speiss from Schladming in Styria was worked up. It contained 45 to 47 per cent. of nickel and 4 to 6 per cent. of cobalt. It was first roasted in a reverberatory furnace with octagonal hearth and eight working doors, the central fireplace being situated under the middle of the bed. After this it was smelted in graphite crucibles with potash and quartz. The crucibles were placed eight in each air furnace, and each contained 35 to 45 lbs. of the roasted coarse speiss, with 30 per cent. potash and 12 per cent. quartz. The heating of this furnace took 3 hours, then the fusion took place after 6 hours more; the crucibles remained 17 more hours in the fire, and then were taken out and emptied. In 24 hours 194 cub. ft. charcoal were used. 100 parts of roasted coarse speiss gave 55 refined speiss with 67 per cent. of Ni, Co and Cu, 2 per cent. of Fe and 31 per cent. of As. The slag was a mixture of arseniates and silicates of cobalt and iron.

At Leogang, in Salzburg,[2] the coarse speiss was roasted in stalls three or four times, and then smelted to a concentrated speiss in blast furnaces with quartz and slag from the first smelting. The latter speiss was subjected to a blast in a Hungarian reverberatory furnace on a quartz bed. The blast was continued with repeated removal of slag and addition of sand until all the iron was slagged. The slag resulting contained cobalt, and was smelted with quartz and arsenic into a cobalt speiss.

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[1] *Berg. und Hütt. Ztg.*, 1878, p. 206. [2] *Ibid.*

c. CONVERSION OF REFINED SPEISS INTO RAW NICKEL

This conversion is effected by a complete roasting of the speiss and subsequent reduction to metal.

a. The Dead Roasting of Refined Nickel Speiss

The object of this is to convert the arsenide of nickel entirely into monoxide. It is done by repeated roasting, the decomposition of any arseniate formed being ensured by the addition of carbonaceous matter, or part of the arsenic may be converted into alkaline arseniate by the addition of saltpetre and soda during the roasting. Again, the two treatments may be combined, and first carbonaceous matter, secondly saltpetre (alone or with soda) added to the speiss during roasting.

Nickel arsenide is oxidised to monoxide and to arseniate, while arsenic trioxide escapes The arseniate may be made to give off some arsenic and form a basic compound by raising the temperature. But in presence of carbon it is reduced to arsenide, which again becomes converted partly into monoxide, partly into arseniate, by oxidation, while more arsenic trioxide is given off. The amount of arseniate present thus diminishes, and in this way, by alternate oxidation, and reduction, all the arsenic is finally removed.

Again, the addition of saltpetre to the charge converts the arsenic into an alkaline arseniate, easily removed by washing with water. By taking advantage of this action the last portions of arsenic and of sulphur are removed, the sulphur as alkaline sulphate. Frequently soda, or soda and salt, is added with the saltpetre. By the action of the salt some arsenic chloride (and antimony chloride from any antimony present) are formed and volatilised.

(Apart from roasting, arsenic may be removed also by smelting the speiss with saltpetre and soda, or smelting it with soda and sulphur, and washing out the salts formed; or it can be removed in the form of sulphide of arsenic by heating the speiss with sulphur in absence of air.)

At Schladming[1] the refined speiss was completely roasted in a furnace, of which the construction may be seen in Figs. 334, 335, 336.[2]

The fireplace *f* lay under the hearth *H*, which was 6 feet 6 inches square. The gaseous products of combustion passed up the perpendicular chimney *k* opening into the heating chamber in the middle of the hearth. They left this latter by four openings *z* at the four corners, which openings served also as working ports, thence into chimney hoods over the corners, and over the arch of the furnace into the chimney *y*.

The charge in the furnace was 4 cwt. of speiss, which was dead roasted in 24 hours, using wood fuel After 20 hours had elapsed, about 45 lbs. of a mixture of equal quantities of saltpetre and soda was added, which converted the arsenic still present into alkaline arseniate. This was dissolved out after the roasting, in a tub with water. The residue consisted of nickel oxide.

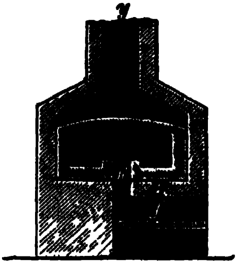

Fig 334

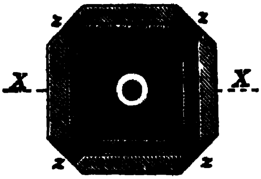

Fig 335.

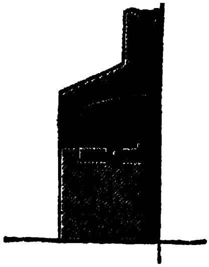

Fig 336

At the George Works at Dobschau, in Hungary, the refined speiss was roasted, in 1867, in a reverberatory with double hearth. Towards the end of the first roasting, pine needles or charcoal dust was added to the mass at intervals of about half an hour. The product was sieved and ground, and then mixed with 10 per cent. of its weight of soda, 5 per cent. of saltpetre, and 10 per cent. of sea salt, and subjected to a second roasting for 4 hours. In this, arsenic and antimony were partly volatilised as chlorides, partly converted into alkaline arseniates and antimoniates. On account of these the mass remained pasty for 2 hours. After the roasting the arseniates and antimoniates were removed by repeated washing with hot water.

[1] *Berg. und Hütt. Ztg.*, 1878, p. 228.

[2] Kerl, *Metallhuttenkunde*, p. 548.

β. Reduction of Dead Roasted Speiss to Crude Nickel

This is done in the same way as the reduction of a completely roasted matte of nickel, given above.[1] If the speiss contains copper, so will the crude nickel. At Schladming in Styria, from 1860 to 1867,[2] the dead roasted and ground speiss was mixed with 4 per cent. of syrup, and made up on a tin plate into cakes weighing 3·7 lbs., 6 inches wide, 10 inches long, and $\frac{1}{8}$ inch thick; these were dried and cut into cubes. The cubes were dried in the sun or in a baking-oven and reduced to metal in crucibles of fire-clay. Each crucible took a charge of 26 to 29 lbs. of the cubes of nickel monoxide, with 3 lbs. of coal dust; 40 crucibles were placed in a round furnace, represented in Figs. 337, 338. *R* is the heating chamber which receives the crucibles; the fireplace is below it. The products of combustion pass from the fireplace *r* through an opening *o* in the middle of the bed, into the heating chamber, thence through 6 flues *z* into a chamber above the arch of the furnace, thence into the chimney *v*.

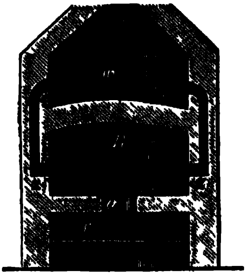

Fig. 337.

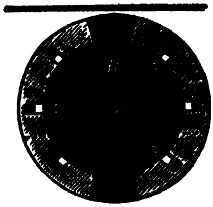

Fig. 338.

The heating of the crucibles, performed with wood fuel, lasted 48 hours. At each operation 7 cwt. of crude nickel were obtained.

B. Extraction of Nickel from Metallurgical Products

Nickel or its alloys can be extracted in the dry way from various metallurgical residues, particularly certain forms of speiss obtained from copper, lead and silver ores which contain nickel as an impurity, often very slight in quantity. Further, coarse or blister-copper frequently contains nickel, which collects in this product if there is but little arsenic in the copper ore; and there are also slags and iron sows containing nickel.

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[1] P. 551.

[2] *Berg. und Hutt. Ztg.* 1878, p. 244.

The speiss is worked up in the same way as the coarse speiss obtained in the extraction of nickel from its arsenical ores. If it contains large quantities of lead, copper and silver, it is sought to separate lead and silver as an alloy (argentiferous lead) and the copper as a matte. Lead may always be removed from the speiss by roasting and reduction, and takes with it the greater part of any silver that may be present. Thus most of the silver is disposed of in the same process. The copper is converted into sulphide by smelting with heavy spar, or with pyrites if that cannot be obtained. There results after these operations a speiss richer in nickel and mostly free from the other metals, and this is worked up by the processes mentioned above.

So, for example, at Freiberg, a speiss containing all three of the above metals served for the extraction of the three, and was smelted several times in a blast furnace with the addition of heavy spar, lead residues and slag, and was converted into argentiferous lead, copper matte, and a speiss containing but little silver, lead and copper. The speiss thus enriched in cobalt and nickel up to 15 or 18 per cent. was smelted in a reverberatory furnace without any previous roasting, with the addition of 50 to 60 per cent. of heavy spar, and 20 to 25 per cent. of quartz; the products were a copper matte containing lead, and a speiss containing 40 to 44 per cent. of nickel, 8 per cent. of copper, and free from iron.

Copper containing nickel is subjected to a blast, which gives a dross containing nickel, and copper free from it. The dross may be smelted in a blast furnace again to coarse copper containing nickel, or it may be smelted into a speiss when large quantities of arsenic and antimony are present. This coarse copper from the dross, called dross or waste copper, gives on refining or subjecting to the blast a second dross richer in nickel and cobalt. By smelting this in a furnace, copper still richer in nickel is obtained. So by the repetition of these processes the final result is a nickel-copper alloy, which is sold to the nickel works.

Or again, the dross may be smelted with pyrites to a matte containing nickel, or with heavy spar and arsenical pyrites to a speiss and a copper matte. Again, nickel can be extracted from coarse copper in the wet way.

The metal is obtained from slags containing nickel without copper by smelting them in blast furnaces with heavy spar or pyrites, yielding a nickel-bearing matte, or with arsenical pyrites, giving a nickel speiss. But if the slag holds copper in quantities worth recovering, the smelting is carried on with arsenical pyrites and either heavy spar or iron pyrites, so as to obtain nickel in a speiss, copper for the most part in a matte. This does not effect a satisfactory separation. It is therefore necessary, in case the separation is very incomplete, to treat again the speiss containing copper and the matte containing nickel with heavy spar and arsenical pyrites.

For example, in Altenau the slags from the refining of dross copper, containing both copper and nickel, were smelted in blast furnaces with iron pyrites and arsenical pyrites to a speiss and a matte of the following compositions:—

	Speiss.	Matte.
Ni and Co.	26·77	6·10
Cu	19·85	37·24
Fe	15·82	20·84
Pb	12·14	16·10
As	12·15	trace
Sb	10·01	0·47
S	4·57	19·25

The speiss was roasted in heaps three times over, and then resmelted in the same way, with 5 per cent. arsenical pyrites, 12·5 per cent. heavy spar, 50 per cent. slag from copper refining, and 50 per cent. slags from lead matting, into a second speiss and matte. Of these the compositions are:—

	Speiss.	Matte.
Ni	35·13	4·37
Cu	17·18	37·45
Fe	8·41	12·68
Pb	6·59	22·81
As	18·65	trace
Sb	10·82	trace
S	2·16	24·48
Co	10·70	—

The speiss was disposed of to cobalt works.

When nickel is to be extracted from iron sows, they may be subjected to a blast in small refining hearths, and the iron oxide resulting slagged with quartz. In this way alloys are ultimately produced containing much nickel and copper; the method was formerly in use at Klefva, in Sweden. Or by using the blast on a small hearth, and strewing nickel, coarse matte or nickel ore on the mass, the nickel will be obtained in a matte. This was practised formerly at the Ringerick Works, in Norway.

At one works in Saxony,[1] iron sows are treated, which contain molybdenum, the composition being 80 per cent. of Fe, 2·5 per cent. of Cu, 2 per cent. of Ni, 1·5 per cent. of Co, 6 per cent. of Mo, 8 per cent. of S. After being broken small they are roasted in a reverberatory furnace and then subjected to oxidising smelting in a similar furnace with quartz as a slagging material; in this way the greater part of the iron is slagged off, and a regulus is obtained, rich in molybdenum, nickel and cobalt. This latter is heated to redness in a reverberatory with saltpetre and soda, so as to form alkaline molybdates. These are removed by lixiviation, and the residue consists chiefly of a mixture of oxides of nickel, cobalt and copper. This is smelted into a speiss with arsenical pyrites.

C. NEW PROPOSALS FOR THE EXTRACTION OF NICKEL FROM ITS ORES, AND FROM METALLURGICAL PRODUCTS, IN THE DRY WAY

Among new dry methods that have been suggested, Mond's requires mention. In this the nickel in ores or residues, in which it occurs as monoxide, is removed as nickel carbonyl [$Ni(CO)_4$], which is decomposed into nickel and carbon monoxide at a higher temperature. Mond discovered that finely divided nickel in the presence of carbon monoxide at a temperature below 150° was converted into gaseous nickel carbonyl. This compound condensed to a colourless liquid, boiling at 43°, and the vapour was decomposed into its constituents on heating to 180°.

According to Mond, nickel monoxide should first be produced by roasting the ores or residues (especially the Canadian pyrrhotite), and this compound reduced to nickel by means of hydrogen, or some other gaseous reducing agent, at a temperature of 350° to 400°. The metal obtained by this method in a state of very fine division should be exposed to a current of carbon monoxide at a temperature of 50°, when the nickel volatilises in the form of nickel carbonyl. The current of gas containing this compound is to be led into closed vessels, in which, when they are heated to 180°, nickel is deposited in the metallic form and exceedingly pure. The carbon monoxide set free can be used again in the process.

This operation, which would seem to be surrounded by many technical difficulties, has been carried out on the large scale in Birmingham. There is no account to hand of the economic results obtained.

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[1] *Berg. und Hütt. Ztg.*, 1878, p. 213.

II. EXTRACTION OF NICKEL IN THE WET WAY

The wet way is especially used at present to extract pure nickel or nickel oxide from speiss and matte containing copper and cobalt. It is most unusual to submit ores directly to such a process, for in the great majority of cases it is cheaper to concentrate the nickel first in the dry way, forming a speiss or matte. This is especially true of ores containing sulphur and arsenic. A great variety of methods have recently been proposed for extracting nickel in the wet way from the ores in which it occurs as silicate (garnierite), though very few of these seem ever to have been applied At present it still seems more profitable with these ores to concentrate the amount of nickel, even although not very high, and to form a matte in the dry way.

We distinguish then:—

A. Extraction of nickel directly from the ores.
B. „ „ from smelting products.

A. EXTRACTION OF NICKEL DIRECT FROM THE ORES

If the ores contain arsenic or sulphur they must be roasted before being treated with solvents. (Sulphuretted ores may be prepared for a wet method by smelting with potassium carbonate and sulphur, as at the Gap Mine, Pennsylvania.)[1] Ores such as garnierite, containing nickel silicate, can be treated direct with solvents. Hydrochloric acid is generally the one used, occasionally dilute sulphuric acid. The latter, however, causes the formation of a precipitate of calcium sulphate afterwards, during the treatment of the solution with carbonate of lime and milk of lime.

Ferric sulphate has been suggested by Emmens[2] (Gossan process) as the solvent for the sulphuretted ores of Canada. According to him the nickel in Canadian pyrrhotite is dissolved out by this reagent, even from the unroasted ore, but the solution of nickel from the roasted ore seems to be very much more rapid. Emmens therefore suggests the roasting of the ore in furnaces, or the weathering of it, and subsequently treating it with ferric sulphate in wooden vats. Nickel is to be precipitated from the liquor as hydrate. The process has not yet been put into practice.

This process has been tried experimentally by the Canadian Copper Company, but not brought into definite use. In the most favourable cases only one-third of the amount of nickel and two-thirds of the copper of the ore are brought into solution by ferric sulphate.[1]

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[1] *Berg. und Hutt. Ztg.*, 1877, p. 300.

[2] *Mineral Industry*, 1892, p. 355.

Macfarlane proposed to convert the nickel of the Canadian sulphuretted ore into chloride by roasting with common salt, and to leach the product with water to dissolve this chloride. Iron was to be precipitated from the liquor by a small quantity of caustic soda, and any copper present by sodium sulphide. Finally the nickel was to be precipitated as hydrate by caustic soda. But nothing is as yet known with regard to the extent to which this method is put into practice.

Ricketts[2] brings nickel and copper into solution as sulphates, and then precipitates the nickel as basic sulphate by alkalies and alkaline sulphates. The basic sulphate is converted into monoxide by strong heating. Then the copper remaining in solution can be deposited electrolytically.

Richardson[3] converts both nickel and copper into chlorides, and separates the two salts by fractional distillation in an atmosphere of hydrochloric acid gas.

The way in which the solution is generally treated is as follows:—

It is first treated with sulphuretted hydrogen or an alkaline sulphide to precipitate copper, bismuth, lead, arsenic and any metals precipitable by these reagents. Then it is treated with chloride of lime to convert the iron into peroxide, which is precipitated by calcium carbonate. With the iron any arsenic present is got rid of as iron arseniate. Next comes the separation of cobalt as sesquioxide by chloride of lime. Finally the nickel is precipitated as nickelous hydrate by milk of lime or soda. The hydrate is converted into oxide by heating to redness, ground up fine, and treated with dilute acid to remove excess of chalk and calcium sulphate.

If copper is to remain with nickel, and an alloy of the two finally produced, the liquid can be treated at once with calcium carbonate, after previously oxidising the iron, and thus removing arsenic and iron. This is as long as the metals of the sulphuretted hydrogen group, other than arsenic, are absent.

Occasionally the nature of the ore renders modifications of these processes necessary. Further, special plans have very recently been elaborated for the treatment of nickel silicate, garnierite in particular, but have come to a very small extent into practical use, and therefore can only be mentioned shortly.

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[1] *Mineral Industry*, 1894, p. 463.

[2] American Patents of Oct. 3, 1893, and Feb. 6, 1894.

[3] American Patent, April 10, 1894.

Formerly arsenical ores of nickel were worked by the wet method in Hungary[1] and in Bohemia; it is now no longer used for these ores. The ores were treated with hydrochloric acid after preliminary roasting (Louyet's process), and the solution was diluted with water, to precipitate the bismuth as basic chloride. Then chloride of lime was added, to oxidise ferrous oxide and arsenious oxide, after which milk of lime precipitated ferric hydrate and arseniate. Copper was precipitated by sulphuretted hydrogen or sulphide of barium, then cobalt as sesquioxide with chloride of lime, and lastly nickelous hydrate by milk of lime.

At Joachimsthal[2] in Bohemia the silver ores containing from 5 to 10 per cent. of nickel and cobalt were formerly roasted in a current of steam. Silver was then separated as metal and nickel, and cobalt arseniates were formed. The roasted product was first treated with dilute sulphuric acid, and then with hot nitric acid. The former dissolved nickel and cobalt arseniates, the latter the silver and the remaining cobalt and nickel. After the silver had been precipitated by common salt the nitric acid solution was mixed with the sulphuric acid solution, and the whole treated with ferric chloride to convert the arsenic into ferric arseniate. Powdered limestone caused the precipitation of ferric arseniate, and from the solution remaining cobalt and nickel were successively thrown down by chloride of lime and milk of lime respectively.

Special proposals to separate nickel from silicates (garnierite and rewdanskite) are as follows:—

Herman[3] heats rewdanskite with sulphuric acid in stoneware vessels until the acid begins to vaporise, lixiviates the mass, oxidises the iron with salt and saltpetre, precipitates it by chalk, and precipitates nickel sulphide by sodium sulphide. This is completely roasted and the monoxide reduced.

Laroche[4] treats garnierite with its own weight of sulphuric acid 56° to 60° B., washes the solid product with warm water, and adds ammonium sulphate in quantity equivalent to the nickel sulphate present, and thus separates crystals of nickel-ammonium sulphate from the solution by evaporating down and cooling. These are dissolved in boiling water, and nickel carbonate precipitated by solution of soda. Instead of ammonium sulphate, an equivalent quantity of alkaline oxalate may be added, and nickel oxalate thrown down from the solution. The precipitate is treated with boiling soda solution at about 110° C., when nickel carbonate is formed together with the alkaline oxalate. The carbonate is reduced to metal, and the oxalate is used over again.

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[1] *Berg. und Hütten. Ztg.*, 1849, p. 800.

[2] Kerl, *Metallhuttenkunde*, p. 554.

[3] *Berg. und Hutt. Ztg.*, 1876, p. 308.

[4] Wagner, *Jahresberichte*, 1879, p. 235.

Rousseau[1] dissolves the mineral in hydrochloric acid, oxidises the iron with chloride of lime and precipitates it with calcium carbonate. Then he precipitates nickel with milk of magnesia. The solution remaining, consisting of magnesium and calcium chlorides, is evaporated down, and he proposes to obtain hydrochloric acid and magnesia from the solid residue by heating in a current of steam.

Kamienski[2] dissolves the ore in dilute hydrochloric acid, oxidises the iron by a current of chlorine, precipitates it with magnesium carbonate, and decants off the warm liquid, and precipitates most of the nickel as carbonate, with soda. Then the solution is again treated with soda in the cold to precipitate magnesia and the rest of the nickel. The solution containing sodium and magnesium chlorides is evaporated down until salt crystallises out. From the remaining liquid magnesium chloride can be separated by evaporation; the latter salt will yield hydrochloric acid if heated to 150° in a current of steam.

Araud[3] mixes the ore into a paste with hydrochloric acid, and heats this in fireproof retorts until the chlorides formed volatilise. They are condensed and dissolved in water. From the solution iron is precipitated by calcium carbonate, and then nickel by milk of lime.

Sebillot[4] has suggested two methods. One is to mix the ore with sulphuric acid and ammonium sulphate, to add water and allow nickel to crystallise out of the solution as sulphate. The crystals are redissolved and nickel precipitated from this solution in the usual way. The second way is to heat the ore with sulphuric acid in a reverberatory furnace, to leach the solid mass remaining with water, precipitate iron by calcium carbonate after oxidising with chloride of lime, then to precipitate magnesium by sodium phosphate, and finally allow nickel sulphate to crystallise out of the lye.

Dixon[5] smelts the ore to a speiss and treats this in the wet way to be subsequently described.

Allen treats the powdered ore with sulphuric acid in the cold, adding some Chili saltpetre; then heats the mass to redness, lixiviates with water, precipitates first iron and chromium by calcined magnesia, then nickel as sulphide by sulphuretted hydrogen. The sulphide is completely roasted and reduced.

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[1] *Berg. und Hutt. Ztg.*, 1878, p. 260.

[2] *Ibid.*

[3] *Loc. cit.*, p. 260.

[4] *Loc. cit.*, p. 260.

[5] *Loc. cit.*, 1879, p. 395.

Christofle[1] has suggested several methods of treating garnierite in the wet way. These all appear to consist chiefly in the smelting of the ores to a matte and treating this as will be subsequently described.

The processes for direct wet treatment of the ore were as follows:—

1. The powdered ore is leached first with dilute, then with strong hydrochloric acid. Iron is precipitated from the solution in strong acid by quicklime or chalk, and then nickel by milk of lime.

2. The powdered ore is heated with concentrated oxalic acid solution, which leaves nickel undissolved. The residue is reduced to obtain nickel. To recover the oxalic acid, the solution is treated with milk of lime and calcium oxalate thrown down, from which oxalic acid is separated by sulphuric acid.

3. The ore is treated with hot concentrated hydrochloric acid, chloride of lime added to the solution, containing excess of acid, to oxidise the iron; nickel oxalate is precipitated by oxalic acid, and the precipitate washed and heated.

4. The ore is treated with hot concentrated hydrochloric acid, chloride of lime is added to the acid solution, iron and aluminium are precipitated by calcium carbonate, nickel is precipitated as sesquioxide by lime-water and chloride of lime.

5. The ore is treated with concentrated hydrochloric acid, iron and aluminium are precipitated by the method of (4), magnesium chloride is added (if not already present in sufficient quantity), and nickel is precipitated with a small quantity of magnesia by quick-lime. The precipitate is washed, dried, mixed with coal, and heated to a very high temperature, when the sulphur is taken up by the magnesia. The nickel then forms in grains and is washed out of the ignited residue.

Herrenschmidt[2] has brought out a process which is said to be in use at the works of the Malétra Chemical Company at Petit Querilly, near Rouen, France. An ore from New Caledonia is employed, with 18 per cent. of manganese dioxide, 3 per cent. of cobalt monoxide, 1·25 per cent. of nickel monoxide, 30 per cent. of ferric oxide, 5 per cent. of alumina, 2 per cent. of limestone and magnesia,

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[1] *Berg. und Hutt. Ztg.*, 1878, p. 259; 1879, p. 188; Wagner, *Jahresberichte*, 1878 p. 233.

[2] Pelleton, *Genie Civil*, 1891, vol. xviii., p. 373; *Engin. and Mining Journal*, 1891, vol. lii., No. 14.

8 per cent. of silica. It is treated with a concentrated solution of green vitriol, which is said to dissolve manganese, cobalt and nickel as sulphates, while ferric oxide remains in the residue. The liquid, after being separated from the residue and allowed to settle, is treated with sodium sulphide which precipitates cobalt, nickel and a small quantity of manganese, as sulphides. The last can be removed from the precipitate by solution of ferric chloride. The solution containing manganese is converted into calcium manganite by treatment with milk of lime in excess and a current of air. This calcium manganite is utilised in the production of chlorine for making chloride of lime (Weldon process). The precipitate which has been freed from manganese, and contains only sulphides of nickel and cobalt, is subjected to roasting in a reverberatory furnace which converts it into a mixture of sulphates. These are dissolved in hot water and then converted into soluble chlorides by calcium chloride. For the separation of the metals, the liquid is divided into two parts. From the first part, they are precipitated as hydrates of protoxides by milk of lime, the precipitate is filtered off, washed into water, and the liquid treated with a current of chlorine and air until the sesquioxides are formed in it. The other half of the solution of chlorides is now added to this sesquioxide precipitate, and steam blown through the liquid for some time. Cobalt sesquioxide remains undissolved, while nickel sesquioxide passes into solution as chloride, and an equivalent quantity of cobalt sesquioxide is precipitated. After the whole of the cobalt has thus been separated, or else the whole of the nickel has gone into solution, the liquid is separated from the residue, and nickel is precipitated from it in the usual way by milk of lime.

Nothing is known yet as to the economic results of this process, which seems rather complicated, and capable of being conveniently put into practice only at Leblanc soda manufactories, which also make chloride of lime.

By the process patented in Germany,[1] Herrenschmidt precipitates iron and copper from the solution containing iron, copper, cobalt and nickel, as sulphates or chlorides, thus:—he precipitates the iron by copper carbonate, and then, after separating this precipitate, the copper by nickel hydrate or nickel carbonate. Lastly cobalt and nickel are obtained from the solution as described above, after this last precipitate has been removed.

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[1] German Patent, No. 68,559.

B. EXTRACTION OF NICKEL FROM SMELTING PRODUCTS

These processes are divided into three groups—those for matte, those for speiss, and those for slags.

1. EXTRACTION OF NICKEL FROM MATTE

Matte, whether unroasted or dead roasted, will dissolve in acids. If unroasted matte is treated with acid, copper sulphide remains behind, and iron, nickel and cobalt dissolve for the most part. It is not possible to remove the whole of the cobalt and nickel from the residue, so that the latter has still to be specially treated for the two metals.

The treatment of unroasted matte with acid is therefore not to be recommended; it is undertaken only exceptionally. The usual method is to dead roast the matte before treating it with acids.

As ignited ferric oxide dissolves very slightly in dilute acid, it is well to raise the temperature as high as possible at the end of the roasting, so that as much iron as possible may remain in the residue. Hydrochloric or sulphuric acid is used as a solvent, the former preferably. If the roasting has been successful, practically no iron dissolves in either acid. Any arsenic present remains in the residue, as ferric or copper arseniate.

The usual method of treating the solution, subject to many variations, is the following:—It is treated with sulphuretted hydrogen or an alkaline sulphide to separate copper, lead, &c. Then iron is oxidised by chlorine or chloride of lime, and precipitated by calcium carbonate. This precipitation must take place in the cold, as above 40° C. an appreciable quantity of cobalt separates out. If copper has not been thrown down as sulphide, part of it now separates as carbonate. If arsenic acid is present it comes down with the iron.

Cobalt is next separated as sesquioxide by chloride of lime. Excess of chloride of lime throws down nickel as well. Potassium nitrite[1] throws down cobalt from a solution neutralised by potash and acidified again by acetic acid, as cobalt-potassium nitrite, and leaves nickel in solution; but it cannot be used to separate cobalt when lime or other alkaline earths are present, for then nickel is precipitated with the cobalt as nickel-potassium-calcium nitrite $K_2CaNi(NO_2)_6$.

If great quantities of cobalt are in solution, and extreme purity of metal is not essential, ammonium sulphate can be used to separate cobalt and nickel. This produces a difficultly soluble double salt with nickel sulphate; an easily soluble one with cobalt sulphate. When the solution is sufficiently concentrated by evaporation, the nickel double salt separates out and leaves the cobalt in solution. The former is converted into nickel monoxide by heating, ignited with soda and saltpetre, and lixiviated. In the heating of the double salt ammonium sulphate can be recovered. Cobalt is precipitated from the remaining solution of cobalt-ammonium sulphate by ammonium sulphide. Cobalt sulphide is roasted, heated with saltpetre and soda, and sent into market as sesquioxide.

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[1] *Pogg. Ann.*, 74, 115; 110, 411; and *Ann. Chem. Pharm.*, 96, 218.

From the solution from which cobalt has been thrown down as sesquioxide by chloride of lime, nickel is precipitated as hydrate or as carbonate by milk of lime or by soda. The precipitate is filtered from the liquid in conical linen bags, and, if calcium sulphate is present, heated with soda, so that calcium carbonate and sodium sulphate are formed. The latter is washed out of the product by water, and the calcium carbonate removed by dilute hydrochloric acid. The decomposition of calcium sulphate by soda can also be conducted in the following way: the precipitate is heated with soda solution, the soda being present in excess, and then the residue of calcium carbonate is washed out with water acidified with hydrochloric acid. If hydrochloric acid has been used as solvent for the nickel, lime can be leached out from the calcined nickel monoxide with the same acid.

The nickel monoxide obtained in this way is reduced to nickel by the usual method.

A direct treatment of matte with acid was formerly in use at the Scopello works in Piedmont.[1] The nickel matte, containing 24 per cent. of Ni, 6 per cent. of Co, 12 per cent. of Cu, 23 per cent. of Fe, and 35 per cent. of S, was treated with hydrochloric acid (33 per cent. of HCl) in stoneware vessels surrounded with water in wooden barrels. Sulphuretted hydrogen was emitted from a tube in the cover of the vessel and was burned. After the matte had been three times treated with acid the liquid was syphoned off from the residue, which consisted of the copper sulphide of the matte and an appreciable quantity of nickel and cobalt sulphides. This was charged into the blast furnace during the smelting of matte or ore. The solution, containing chlorides of iron, nickel and cobalt, was first allowed to settle, and then evaporated to dryness in a cast-iron pot heated from above. The residue after this evaporation, a pulverulent mixture of the three lower chlorides, was heated in a reverberatory for 3 or 4 hours, with continual stirring, during which process part of the iron volatilised as chloride, part remained as ferric oxide. After this treatment the mass was put into a vat with water, and then the remaining iron was oxidised by chloride of lime and precipitated by powdered marble. When the solution was clear, cobalt was thrown down by chloride of lime, nickel by milk of lime. The precipitates so obtained, cobalt sesquioxide and nickelous hydrate, were washed in woollen sacks until ammonium oxalate caused no cloudiness in the wash water. Then the two oxides were heated for 12 hours, and afterwards washed with acidified water.

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[1] *Berg. und Hutt. Ztg*, 1878, p. 229.

The treatment of roasted matte with acids used to be, or is still, carried on at the Isabella works at Dillenburg, at the Victoria works in Silesia, at Schneeberg in Saxony, and at the Christofle works at St. Denis.

At the Isabella works nickel was produced in the wet way between 1848 and 1857; from 1857 to 1860 both nickel and the copper-nickel alloy. The methods for each are briefly described below.[1]

(*a*) In the earlier process the red-hot concentrated matte was quenched in water to render it brittle, then pulverised, and sieved. The powder, in quantities of 3 cwt., was subjected to roasting in a reverberatory furnace in order to remove sulphur and oxidise iron.

The roasted product was mixed to a thick paste with sulphuric acid (60° B.) in vats, and then gently heated for two hours in a reverberatory furnace; during which time any ferrous sulphate was converted into ferric, and any excess of acid was driven off. The dry mass was treated with water to dissolve the sulphates, the solution then containing iron, copper and nickel sulphates. The first step was to precipitate iron and copper by calcium carbonate. For this purpose the liquid was raised to the boiling point in a copper boiler, and finely powdered calcium carbonate added by ladles full, by which iron and copper were thrown down as basic carbonates, and calcium sulphate with them. As iron comes down before copper, the precipitant was added only as long as iron was present in the solution, and then this precipitate, containing both iron and copper, was removed. A little nickel was always thrown down with copper, but in this way the presence of nickel in the first precipitate was avoided. It consisted only of iron and copper basic carbonates with calcium sulphate, and could be worked up into copper matte or copper. The filtrate from this precipitate was boiled up with a fresh quantity of calcium carbonate, and thus copper thrown down with a small amount of nickel. This precipitate was added in the concentration of nickel

[1] Schnabel, *Preuss. Zeitsch.*, 1865, p. 109.

matte. The filtrate was treated with milk of lime to precipitate nickel hydrate. To remove calcium sulphate from this precipitate it was dried and heated with soda in fire-clay crucibles, whereby calcium carbonate and sodium sulphate were formed. The latter was washed out by water, the former by hydrochloric acid. The nickel monoxide was reduced in the usual way, and formed cubes with the composition:—

Ni	98·29	per cent.
Cu	0·24	„
Fe	0·81	„

(*b*). According to the later method a coarse matte of average composition:—

Ni	13	per cent.
Cu	19	„
Fe	35	„
S	33	„

was converted into a concentrated matte of average composition:—

Ni	24	per cent.
Cu	39	„
Fe	12	„
S	25	„

This latter by oxidation under a blast on a hearth produced a matte composed of:—

Ni	35	per cent.
Cu	43	„
Fe	2	„
S	20	„

This last matte was dead roasted, and then treated first with hydrochloric, then with sulphuric acid. The former dissolved the greater part of the copper and nickel, but not any iron present as ferric oxide; the proportion of the metals dissolved was 7 parts copper to 1 nickel. Both were precipitated from the solution by milk of lime. The precipitate was compressed, dried, and reduced to copper-nickel alloy, after the removal of the calcium sulphate.

The residue after treatment with hydrochloric acid (about 40 per cent. of the roasted matte) was twice treated with sulphuric acid in the way described above, whereby the greater part of the remaining copper and nickel and a portion of the iron passed into solution. The residue finally remaining was re-roasted. Iron was precipitated from the solution by calcium carbonate at a temperature of 55°C., and then copper as basic carbonate at 70°C. by the same agent. A little nickel accompanied this copper, increasing in amount with the amount of copper. In order to make this quantity of nickel as small as possible, it was sought always to dissolve as much copper as possible in the first treatment with hydrochloric, acid.

The precipitate of basic carbonates of copper, nickel and iron was dissolved in hydrochloric acid. Copper and nickel were precipitated from this by milk of lime. This precipitate was first purified and then reduced to copper-nickel alloy. From the sulphuric acid solution still remaining, containing nickel sulphate with a little copper sulphate, the same agent—milk of lime—precipitated nickel hydrate, which was filtered off, compressed, and then dried.

The removal of calcium sulphate from these oxides (the copper oxide containing 8 per cent., the nickel monoxide 15 per cent.) was achieved by washing them with dilute hydrochloric acid after very strong heating. This acid removed the calcium sulphate, but no nickel monoxide, and very little copper oxide if the heating has been carried to the necessary temperature. After the acid had been used for washing, any portion of either metal present was removed from it by precipitation with milk of lime. This precipitate served to neutralise acid solutions which were about to be treated with calcium carbonate.

The oxides were reduced to metal in the usual way. The reduction of the nickel monoxide required 3 hours in time and a strong white heat, while that of the copper oxide containing a little nickel was accomplished at a lower heat in an hour and a half.

Metallic nickel was sent into the market in cubes; the cubes of the copper alloys were melted on refining hearths, taken off in discs, and sold in that form to the Argentan Works. At a later period the copper mixed with nickel oxide was reduced on a refining hearth with two tuyeres, and a copper-nickel alloy with 73 per cent. of nickel obtained.

The metallic nickel obtained in this way had the following composition:—

	I.	II.
Ni	96·29	96·17
Cu	0·41	2·17
Fe	0·98	0·45

The coarse copper obtained from the residues containing copper (from the solution of the precipitates in hydrochloric acid) had the following composition:—

	Ni.	Fe.	Cu.
The middle disc of the hearth	0·99	0·99	98·82
The lower disc of the hearth	0·44	0·80	99·06

Genth made the observation that the small black crystals that form on the upper discs in the hearth during the refining consist of nickel monoxide.

At the Victoria Works in Silesia[1] the concentrated nickel matte was dead roasted, then part of the copper oxide leached out with warm dilute sulphuric acid, and then the residue, washed, dried, ground fine and roasted, was reduced to a copper-nickel alloy containing 80 per cent. of nickel. Any nickel in the sulphuric acid solution was thrown down by copper oxide, and the solution was used to produce blue vitriol.

At Schneeberg, in Saxony, hydrochloric acid was used, instead of sulphuric, to dissolve copper oxide and sulphate out of the roasted matte. The method of working up the residue was the same as at the Victoria Works

At the Christofle Works at St. Denis,[2] the matte obtained by smelting garnierite with gypsum was ground, roasted repeatedly in long-bedded calciners about 33 ft. long, and then treated with hydrochloric acid in stoneware vessels holding about 19 gallons, standing in water. The action was increased by heating this water by steam. The solution was poured into wooden vessels. In these iron was first oxidised, then precipitated by calcium carbonate. Air was blown through to help the action, and served also to agitate the whole mass. It was poured into wooden vessels in which the precipitate settled, and then the clear liquid was drawn off into other vessels in which nickel was precipitated by milk of lime. The hydrate was dried, washed, dried again, and then reduced to metal.

2. EXTRACTION OF NICKEL FROM SPEISS

The speiss is roasted dead, and then treated in the same way as dead roasted matte. In this roasting carbonaceous matter is mixed with the material to ensure the removal of arsenic.

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[1] *Berg. und Hutt. Ztg.*, 1877, p. 300; 1878, p. 245.

[2] Knab, *Metallurgie*, p. 560.

At the George Works at Dobschau, in Hungary,[1] speiss of the composition:—

Ni	37	per cent.
Co	13	„
Cu	2	„
Fe	9	„
As	38	„
S	1	„

was stamped, and then roasted in wood fired reverberatory furnaces in quantities of 6 cwt. The time of roasting was 12 to 14 hours. At the end of this time 65 to 90 lbs. of sawdust or coal dust were added to the roasted product, which reduced the arsenic acid formed to arsenious acid and arsenic. The latter burns again to trioxide. The roasted product was then treated with sulphuric acid. From the liquid thus obtained, iron and part of the copper were precipitated by boiling with calcium carbonate. Cobalt sesquioxide was then thrown down by chloride of lime, and nickel hydrate by milk of lime. These oxides are dried, washed with acidified water, ground, and sold to the smelting works in Saxony.

At Saint Benoit, near Liege,[2] speiss containing 45 per cent. of nickel was treated with concentrated hydrochloric acid at 80°C. Iron was precipitated from the solution in the usual way, and then copper by calcium sulphide. Next cobalt was precipitated by chloride of lime, and lastly nickel by milk of lime.

Dixon,[3] whose process has not yet come into general use, smelts garnierite with the addition of arsenical materials into a speiss, which is then dead roasted, and treated with hydrochloric acid. Into this solution chlorine is led to oxidise the iron, and the latter precipitated by the careful addition of nickel monoxide. Then cobalt is obtained as sesquioxide by leading more chlorine through the liquid, and adding more nickel monoxide. The solution containing the nickel combined with chlorine is evaporated. The solid mass obtained is converted into nickel monoxide by strongly heating in a current of steam, or into metallic nickel by heating in a current of hydrogen. A little nickel precipitates with the cobalt sesquioxide, and is to be removed by leaching it with dilute hydrochloric acid.

At the works in Birmingham, England,[4] the completely roasted speiss is treated with hydrochloric acid. Iron is first oxidised, then precipitated as arseniate by neutralising the solution and warming it; the methods of this oxidation and this neutralisation are not mentioned. Copper is then thrown down by sulphuretted hydrogen. Finally the usual precipitants are used for cobalt and nickel.

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[1] *Berg. und Hütt. Ztg.*, 1878, p. 229.

[2] *Loc. cit.*

[3] *Berg. und Hutt. Ztg.*, 1879, p. 395.

[4] Phillips, *Elements of Metallurgy*, p. 415.

3. EXTRACTION OF NICKEL FROM SLAGS

In the dry method, slags containing nickel are added to the charge in the smelting of ores and mattes.

If such slags are obtained as by-products in the smelting of copper they can be directly treated in the wet way, or can also be smelted into a copper-nickel alloy, which can be subjected to wet treatment. The treatment of the slags can be carried on in the same way as has been described for silicate of nickel and magnesium.

In Mansfeld[1] the slags containing nickel from the refining of copper were smelted in a blast furnace into black copper. This was granulated, refined, and then treated with dilute sulphuric acid in the presence of air. The solution was fractionally crystallised; copper sulphate separated first, and after it had been removed the liquor was evaporated to a certain point, when a mixture of the sulphates of iron and copper crystallised out. Further concentration and crystallisation yielded a mixture of copper and nickel sulphates. (According to von Hauer, if there is excess of copper sulphate in the solution, this salt will first crystallise out pure, and afterwards a copper-nickel-cobalt sulphate of the formula $CuSO_4+(CoNi)SO_4+21H_2O$. If there is excess of either nickel or cobalt sulphate or of both, this compound will crystallise out first, and the excess of these two sulphates will remain in the mother liquor.)

The copper-nickel sulphate, if free from iron, was heated in a roasting furnace to remove sulphuric acid. The residue, consisting of oxides, was leached with water and dried, and then reduced in a Sefstrom furnace to an alloy with 40—68 per cent. of Cu, 30—59 per cent. of Ni, 1·1 to 1·8 per cent. of Co, 0·5 to 1·3 per cent. of Fe, and 0·07 to 0·34 per cent. of S. This was melted on a refining hearth of graphite, with two tuyeres, and taken off in discs.

Herter[2] has proposed to heat a complex sulphate, such as the above, but containing iron, in a reverberatory furnace, and to treat the mixture of oxides so obtained with dilute sulphuric acid, which will dissolve nickel and copper, but not iron. From the solution coppe and nickel are to be precipitated by soda, the resulting basic carbonates heated to form oxides, and the latter reduced.

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[1] *Berg. und Hutt. Ztg.*, 1859, p. 371; 1860, p. 501; 1861, p. 67; 1862, p. 160; 1846, p. 58; 1865, pp. 146, 386.

[2] *Berggeist*, 1865, No. 20.

III. Extraction of Nickel by Electrolysis

Very few communications on this point have been made public. Extraction of nickel from ores by electrolysis seems up till now to have been performed only experimentally, but the method has been used for metallurgical products, particularly upon alloys of copper and nickel.

If ores are to be worked, they must be dissolved outside the electric circuit, as they are such bad conductors.

High potentials are necessary to deposit nickel from solution, and these will cause most other metals to be precipitated. It is therefore very difficult to obtain a thick deposit of nickel. Whilst thin deposits of nickel are unexceptionable, a brittle crumbling metal is obtained as the thickness of the deposit is increased. The strength of current for thick deposits of nickel is shown by the results of experiment to be between 3·5 and 8·5 ampères per square foot, with a potential of 3 to 6 volts, according to the nature of the liquid. According to Borchers,[1] in using the salts of cresol-sulphonic acid and insoluble anodes, 5·5 ampères per square foot, and 2 to 2½ volts are necessary. The metal thrown down from such a solution is 0·012 to 0·016 in. thick, brittle and unsightly. According to Brand,[2] to deposit nickel from a solution of the sulphate saturated with ammonia, with a carbon anode, a potential of 2·4 volts, and a current of 2·8 ampères per square foot is necessary. The same potential is necessary if an iron anode is used instead. A current of 1 ampère separates 16·83 grains of nickel in an hour. To separate 1 kg. nickel in an hour, 914·9 ampères would be necessary. The energy necessary for this is

$$24 \times 914{\cdot}9 \text{ Watts} = \frac{2195{\cdot}8}{75 \times 9{\cdot}81} = \frac{2195{\cdot}8}{735} = 2{\cdot}99 \text{ h.p., or taking into}$$

account a 12 per cent. loss of energy in the conversion of mechanical work into electricity, and a 25 per cent. loss in the current (through waste heat, bad connections, &c.),

$$= \frac{2{\cdot}99}{0{\cdot}88 \times 0{\cdot}75} = 4{\cdot}48 \text{ h.p.}$$

At the rate of 2 kg. of coal for 1 h.p. per hour, 9 kg. coal will be necessary to deposit 1 kg. nickel from the solution described.

[1] *Elektrometallurgie*, p. 103.

[2] Dammer, *Chem. Technologie*, vol. ii., p. 27.

As is stated on page 209, the loss of energy in the latest engines is considerably less than the above. The consumption of coal for one horse-power can be reduced in the newest steam engines to between 1 and 1·5 kg.

Refining of nickel by means of an electric current, as is done with coarse copper with excellent results, is not easily practicable because the strength of current mentioned as necessary to deposit nickel, deposits also the other metals from which it is to be separated.

If nickel is to be separated from its alloys with copper, it is the copper which is deposited from an acidified electrolyte on the cathode, while the nickel passes into solution, because copper is deposited by a weaker current than nickel. After purifying the solution from other metals, especially iron, which may be precipitated by various reagents, nickel is deposited from the solution by the use of insoluble anodes.

Solutions from which nickel is to be deposited must be alkaline. Dr. Böttger[1] has employed the double sulphate of nickel and ammonium as electrolyte, and investigated, in a series of researches, the conditions under which nickel will be deposited as a lustrous white metal. By the use of such electrolytes metals can be covered with a firmly adherent coat of nickel, but it is not possible to obtain it in a thicker deposit.

The extraction of nickel from its ores was practised at the Editha Smalt Works in Silesia. Nickel was deposited by a current from an ammoniacal solution containing caustic soda.

Extraction of nickel from smelting products was proposed by André in 1877.[2] The substances containing nickel,—matte, speiss, or alloys,—were to be cast into anode plates, and suspended in dilute sulphuric acid. For the cathodes copper or carbon plates were suggested. The current should be so regulated that only the copper in these substances separated out on the cathodes, while nickel dissolved in the electrolyte. To remove the last portions of copper from this, a carbon anode should be introduced after the disappearance of the original one. Thus the last of the copper is deposited from the acid solution, which now should contain only nickel sulphate with some iron sulphate.

To remove the iron the solution should be made ammoniacal, and evaporated down in leaden pans in a current of air, so that the iron may be precipitated as ferric hydrate. The liquid filtered from this consists of nickel sulphate only, and may be worked up for the crystallised salt, or the monoxide, or metallic nickel. The last may be obtained by precipitating the hydrate or carbonate, and reducing as has been already described, under wet treatment, or the electric current may again be used. In the last case the solution is made ammoniacal. Carbon or nickel plates, or copper plates covered with graphite are to be used as cathodes. Iron or zinc plates are recommended as anodes, so as to avoid polarisation.

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[1] *Journ. für Pract. Chemie*, vol. xxx., p. 267.

[2] German Patent, No. 6048, Nov. 1, 1877.

It should be noticed, however, that iron or zinc is not adapted for the anode. The iron plates are quickly covered with oxide, and are not depolarisers in that condition. Zinc continues to depolarise because it dissolves, but then it is present in the solution, and is deposited on the cathode with nickel. Under these conditions it will, without doubt, be found necessary to use carbon for the anodes. Borchers recommends as depolariser the cresol already referred to under the electrolysis of zinc solutions. The author is not aware which means of depolarising is now in most common use in the electrolysis of nickel solutions.

Stahl[1] proposes a similar method for extracting nickel from coarse copper. This is melted in a reverberatory furnace, the hearth of which is of basic material, and oxidised to get rid of iron and arsenic, until nickel begins to pass into the slag. Then it is poled and cast into anode plates. These are to be subjected to electrolysis in order to separate the copper, sulphuric acid being the electrolyte, and sheets of copper the cathodes. The current is regulated so that only copper is deposited on the cathode from the acid solution, whereas nickel, iron and small quantities of arsenic pass into the solution, while silver, lead, antimonic acid, antimony oxide, arsenic acid and copper sulphide form a thick mud, which falls to the bottom of the liquid. The separation of the last portions of copper from the solution is performed with carbon anodes as in André's process. Fresh anodes may also be inserted as required in order to obtain by itself the copper which is rendered impure by simultaneously deposited arsenic.

Chloride of lime is next added to the warm solution containing iron and nickel, to convert iron into ferric sulphate; and then slight excess of soda is added to the acid solution, and this is heated until the whole of the iron is thrown down as basic ferric sulphate. This precipitate is removed by filter presses, and the liquid used to make nickel sulphate, monoxide or metal. If metal is to be deposited by electrolysis, the solution is made ammoniacal; dense carbon forms the anode, a sheet of nickel or a sheet of copper, covered with graphite, the cathode.

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[1] *Berg. und Hütt. Ztg.*, 1891, p. 270.

If nickel monoxide is to be produced from the copper-nickel alloy, the copper is still deposited by electrolysis in the way described, and nickel dissolved. Then the monoxide is obtained just as in the wet treatment.

Hoepfner[1] proposes to obtain from the material containing nickel as produced by the above wet treatment, a pure neutral solution of nickel; to acidify this with a weak, badly conducting oxy-acid (such as citric or phosphoric acid), and then to electrolyse with an insoluble anode. The anodes dip into cells filled with a solution of the chloride of an electropositive metal. Vertically rotating or oscillating discs of metal are used as cathodes. The deposition of spongy material is prevented by movable brushes or rubbers. The electrolyte is kept in constant motion by pumps.

Instead of insoluble anodes, soluble or partially soluble ones may be used. The material for such can only be of metals which are more electropositive than nickel (such as zinc), and will not be deposited with the nickel. (These methods are proposed also for the extraction of cobalt, zinc, lead, tin and copper.)

The writer is not yet acquainted with any case of actual employment of the process.

A process has been suggested by the firm Basse and Selve in Altena,[2] which consists first in adding certain organic bodies to neutral or slightly acid solutions containing nickel, cobalt, iron and zinc, such as will prevent the precipitation of their oxides by alkalies. Such are acetic acid, citric acid, glycerine and dextrose. Then the solution is made alkaline by soda or potash lye, and subjected to electrolysis with a current of 2·8 to 9.3 ampères per square foot. Then iron, cobalt and zinc are deposited on the cathode, while nickel either remains entirely in the liquid or comes down partly as hydrate, according to the strength of the alkaline solution. The precipitation of the hydrate occurs if the current is continued for long. The solution then contains nickel free from the other metals, and ammonium carbonate is added to it in such a quantity as to form carbonate of all the free alkali; then it is subjected to electrolysis. Nickel is deposited on the cathode with a bright surface.

Nothing is known as to the practical introduction of this process. There is a process at the works at Balbach, near Newark, for producing nickel salts from Canadian smelting products, but it is kept secret.

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[1] English Patent, No. 13,336, of 1893.

[2] German Patent, No. 64,251.

IV. REFINING OF COARSE NICKEL

Although formerly coarse nickel contained only 60 to 90 per cent. of pure nickel, at the present time a metal can be obtained from the most diverse ores with 98 to 99 per cent. of pure nickel, and containing only very small quantities of impurities—cobalt, copper, iron, zinc, sulphur, arsenic, silicon, carbon, magnesium

The composition of one of the earlier samples of coarse nickel is shown by the following analyses:—

	Joachimsthal per cent.	Klefva per cent.	Schladming per cent.
Ni	86·5—71·4	83·0—90	86·7—88
Cu	trace—18·9	1·3— 0·2	1·8— 1·9
Fe	0·2— 1·3	0·2— 0·4	1·8— 1·9
Co	0·9—12·0	5·5—11·2	6·8— 7·4
As	0·0— 0·6	—	0·7— 0·8
Na	—	0·9— 0·2	—
S	trace— 0·1	0·7— 1·4	—
SiO_2	0·0— 3·5	0·7— 0·9	0·0— 1·0
Residue	0·6— 1·6	—	0·0— 0·8

Two of the later samples of coarse nickel are composed as follows:—

	Iserlohn per cent.	New Caledonia per cent.
Ni	99·6	0·98
Cu	0·2	—
Fe	0·2	—
C	0·3	0·13
Si	—	0·50
Mn	—	1·63

The separation of impurities has already been attempted in the production of coarse nickel, by obtaining a nickel monoxide as pure as possible. The removal of impurities at a later stage by smelting the coarse nickel with oxidation is only possible when they are more easily acted on by the oxygen of the air than nickel is (such as silicon, carbon and iron). Thus the processes of Wharton in Philadelphia, and of von Bischoff in Pfannenstiel, aim at removing carbon and silicon by a sort of puddling process. At the metal-ware manufactory of Berndorf near Vienna, carbon is removed by soaking cubes of nickel, reduced at a moderate heat, in a 4 per cent. solution of alkaline manganate or permanganate,[1] and then fusing at a high temperature. A metal capable of being hammered and rolled is obtained. Garnier[2] removed iron from coarse nickel containing large quantities of it—such as is obtained by the direct smelting of garnierite—by fusion in a Siemens furnace with quartz as a flux. He has also suggested a reverberatory furnace

[1] German Patent, No. 28989.

[2] *Berg. und Hütt. Ztg.*, 1878, p. 245; 1879, p. 137.

with a bed of powdered limestone.[1] In this method carbon dioxide is set free and serves as an agitator, and sulphur is said to be removed from the nickel by the excess of lime and coal. Since the working of the New Caledonian ores into a matte, these methods, which seem hardly to have passed the experimental stage, have fallen into disuse.

At present the object always is to work up coarse nickel obtained by the processes described, into a compact malleable metallic nickel. Pure nickel oxide is worked so as to give the same product, after reduction. The method consists in fusing the metal in crucibles, and removing from the molten mass, by selected fluxes, nickel monoxide, carbon monoxide, and nickel cyanide.

Nickel monoxide dissolves in molten nickel just as ferrous and cuprous oxides in their corresponding metals. It makes the nickel brittle.

Carbon monoxide is readily absorbed by molten nickel, and makes the metal spongy.

Cyanide of nickel, which, according to Fleitmann, may be formed in the molten metal, makes it brittle.

Of the methods described below for the removal of these injurious impurities, the one suggested by Fleitmann of adding magnesium has proved the most effective.

By the addition of magnesium to the molten metal, nickel monoxide and carbon monoxide are reduced to nickel and carbon respectively. Nickel cyanide is decomposed, nickel being set free and volatile magnesium cyanide formed.

To refine the nickel it is fused in crucibles of graphite, lined with burnt fire-clay; these hold between 33 and 90 lbs. of nickel. The same sort of crucible is used for the production of pure nickel from pure nickel oxide. The graphite crucibles used in the Orford Works are 18 inches high and 14 inches wide at the top, and hold about 80 lbs. of monoxide with 16 per cent. of coal for reduction.

It is not advisable to add fluxes in fusing nickel, for they attack the crucibles strongly.

At the Westphalian Works[2] the crucibles, when filled with coarse nickel, are first heated in a wind furnace with coke fuel, and then placed in a furnace built on the Sefström principle, urged by an air-blast. Each of these latter furnaces takes only one crucible.

After the nickel is melted, which is said to take about an hour and a half, a small quantity of magnesium is added, and the metal poured. The magnesium is kept immersed by the help of a bar of pure nickel or fire-clay.

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[1] *Stahl und Eisen*, 1883, p. 518.

[2] *Oesterr. Zeitschrift*, 1894, p. 326.

Fleitmann, the discoverer of the purifying action of magnesium, added at first ⅛ per cent. of magnesium to produce ductile castings,[1] but afterwards he diminished this quantity by using magnesium alloys instead of magnesium, especially the alloy with nickel. When zinc is present in the metal to be purified, to the extent of 4 or 5 per cent., the least addition of magnesium is necessary. Such nickel may be formed by the reduction of the oxides of zinc and nickel intimately mixed. With this $\frac{1}{20}$ per cent. of magnesium is enough; it makes the metal very ductile, and also gives it the power of being welded to itself, or to iron and steel. In consequence of this property it can be made into nickel plated sheets 0·004 inch thick.

The quantity of magnesium can be still further reduced if reducing gases, such as hydrocarbons, hydrogen, or carbon monoxide, are first blown through the molten metal.

In the following analyses by Knorre and Pufahl may be seen the composition of three kinds of nickel before and after the addition of magnesium. These were melted at the works of Basse and Selve in Altena, in graphite crucibles lined with fire-clay, each containing about 70 lbs. About 1⅛ oz. of magnesium was added to each pot; the nickel obtained could be forged.

COMPOSITION OF ORIGINAL SAMPLES.

	I	II	III
Nickel	97·87	97·90	98·21
Cobalt	1·45	1·25	1·19
Iron	0·45	0.50	0·25
Copper	0·10	0·07	0·07
Silicon	0·19	—	—
Silica	—	0·19	0·24
Carbon	trace	trace	trace
Sulphur	0·05	—	trace
	100·11	99·91	99·86

COMPOSITION AFTER ADDITION OF MAGNESIUM.

	I.	II.	III
Nickel	98·24	97·76	98·38
Cobalt	1·09	1·33	1·04
Iron	0·36	0·60	0·32
Copper	0·10	0·09	0·07
Silicon	0·06	0·10	0·07
Magnesium	0·11	0·11	0·12
	99·96	99·90	100·00

Instead of magnesium there are other substances that can be employed to remove the same injurious impurities in nickel, but all seem to have been entirely surpassed by magnesium. Amongst these are black flux and coal, aluminium, calcium, calcium-zinc, manganese, phosphorus, potassium ferrocyanide, and ferrous cyanide.

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[1] German Patents, Nos. 6365, 7569, 9405, 13,304, 14,172, 23,500, 28,460, 28,924.

At the Berndorf Works, black flux and coal were used at one time. The vapour of potassium seems to be set free and to act as a reducing agent.

Aluminium appears to be less active than magnesium. Calcium and calcium-zinc should act energetically, but are more expensive than magnesium.

Manganese, suggested as a purifier by Garnier in 1876 seems to have been thought well of at the works of H. Wiggin and Co., in Birmingham, where it was added in quantities of 1½ to 3 parts to 100 of the metal before casting; an addition of more than 5 per cent. is said to make nickel hard. Manganese peroxide can also be mixed with the nickel oxide before reducing. At the Basse and Selve Works about 2½ to 3 per cent. of the peroxide is said to be added to the nickel oxide before it is made into cubes.[1] Thus manganese peroxide is reduced to metal in the subsequent reduction. The metal combines with oxygen and will be separated in the slag.

Fleitmann[2] uses manganese to separate sulphur from nickel Coarse nickel or the monoxide is melted with coal in a cupola furnace and then the liquid metal run into a Bessemer converter. To this is added manganese or a manganese alloy, by which the sulphur is carried into a slag. After this has been removed from the surface of the molten mass, air is blown through to oxidise carbon, manganese and iron. After the carbon has burned out, a mixture of air and oxygen, or oxygen alone, is blown in, so as to increase the temperature of the whole and ensure the complete combustion of the iron. Finally the excess of oxygen now present in the liquid metal is said to be removed by a fresh addition of manganese-nickel, or by powdered charcoal, or by gaseous reducing agents, carbon monoxide, a hydrocarbon or hydrogen.

Nickel obtained by these means is said to be very good for rolling and hammering.

Phosphorus was tried as early as 1855 by Ruolz and Fontenay. It had the power of combining with more oxygen, weight for weight, than any of the other agents. It has also, according to Garnier, the property of increasing the hardness of nickel at the expense of its malleability, if more than the three-thousandth part is present. Garnier, therefore, has adopted a phosphor-nickel with about 6 per cent. phosphorus. He prepares this alloy by fusing a mixture of nickel, coal, calcium phosphate, and silica.

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[1] German Patent, No. 25,798.

[2] German Patent, No. 73,243, 20 July, 1892.

According to Manhes,[1] sulphur is removed from coarse nickel by smelting it in a regenerative reverberatory furnace, with a mixture of lime and calcium chloride or chloride of lime, on a hearth with a basic lining. This mixture must be laid in a fairly deep layer on the hearth, and on top of it the metal to be refined, in granulated form, and mixed with lime and the chloride of calcium or chloride of lime. At a sufficiently high temperature part of the sulphur passes off as dioxide and the rest goes into the slag as basic sulphide.

According to Wedding the addition of magnesium is necessary for a compact forgeable metal.

Compact metal may be also obtained if the monoxide is mixed with powdered charcoal, heated to the reduction point in graphite crucibles, and then fused.

Molten nickel is poured into cast-iron moulds. If it is to be used in making alloys, it is granulated by pouring it into water.

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[1] German Patent, No. 77,427, 21 Jan., 1894.

COBALT

PHYSICAL PROPERTIES

Cobalt possesses a reddish-grey colour and considerable lustre: it is ductile at a red-heat, but at ordinary temperatures it is hard and brittle, and is suitable for the manufacture of cutting tools, on account of its hardness. It has a granular fracture. Its specific gravity is said to be between 8·5 and 8·9; that of the metal reduced by hydrogen is 8·957, according to Rammelsberg. It is magnetic, melts between 1600° and 2000° C., and cannot be volatilised. Regnault gives the specific heat as 0·10696.

THE CHEMICAL PROPERTIES OF COBALT AND OF ITS MOST IMPORTANT COMPOUNDS

Massive cobalt does not change in either damp or dry air, but the metal which has been reduced in hydrogen at the lowest possible temperature, or that which has been prepared at a low temperature from the oxalate, is pyrophoric. On heating cobalt in oxygen it burns with a red light forming the oxide: at a red heat it decomposes water.

It dissolves slowly in hydrochloric and sulphuric acids with liberation of hydrogen, and easily in hot dilute nitric acid, forming in each case a solution of the corresponding cobaltous salt. It absorbs carbon when heated with it; combines directly with sulphur, the halogens, phosphorus, arsenic, antimony and silicon; can be precipitated by the electric current from its solutions, and in other respects resembles nickel very closely in its properties.

OXIDES

It forms three oxides:—Cobaltous oxide CoO, cobaltoso-cobaltic oxide, Co_3O_4, and cobaltic oxide, Co_2O_3, all of which are black, and can be reduced to metal by carbon or hydrogen at a high temperature. Cobaltic oxide combines with water to form a dark-brown powder, the hydrate $Co(OH)_6$, which when heated passes successively into Co_2O_3, Co_3O_4, and CoO. The principal salts of cobalt are those derived from cobaltous oxide.

COBALTOUS SULPHIDE, CoS,

is obtained as a blackish-brown precipitate when aqueous solutions of cobaltous salts are treated with an alkaline sulphide. This precipitate is insoluble in dilute hydrochloric acid.

COBALTOUS SULPHATE, $CoSO_4+7H_2O$,

forms a soluble double salt with ammonium sulphate which, like the corresponding nickel salt, serves for the electrolytic deposition of the metal.

Potassium nitrite when added to solutions of cobaltous salts precipitates *potassium-cobaltoxy-nitrite*, $KNOCo_2(NO_2)_6$, as a yellow crystalline powder.

The so-called *cobaltamines* are compounds of cobaltic chloride with varying amounts of ammonia, and are formed by the oxidation of ammoniacal solutions of cobaltous chloride. Roseocobaltous chloride, $Co_2Cl_6.10NH_3+2H_2O$; Purpureo-cobaltous chloride, $Co_2Cl_6.10NH_3$; Luteocobaltous chloride, $Co_2Cl_6.12NH_3$ are some of these bodies. When heated, they are all converted into pure metallic cobalt, and have been proposed for its manufacture.

COBALT ORES

The ores of cobalt which serve for the production of the oxide or *smalt* are *speiss-cobalt*, *cobaltine*, *cobalt-pyrites* and *earthy cobalt.* The other minerals in which cobalt occurs possess a mineralogical rather than a metallurgical interest.

Speiss-cobalt, *smaltine*, or *tin white cobalt*, $CoAs_2$, which, when pure, contains 28·2 per cent. of cobalt, occurs in Saxony at Freiberg, Schneeberg and Annaberg; in Prussia at Riechelsdorf; in Bohemia at Joachimsthal; in Hungary at Dobschau; at Tunaberg in Sweden; at Allemont in France; in Cornwall, and in the State of Missouri, U.S.A.

Cobaltine, *bright white cobalt* or *cobalt glance*, CoAsS, contains when pure 35·5 per cent. of cobalt, but usually a portion of the cobalt is replaced by nickel and iron. It is found at the following places:—In Sweden at Tunaberg, Riddar-hyttan, Gladhammar and Vena near Annaberg; in Norway at Skutterud; in England at Botallack, Cornwall; in Germany at Querbach (Silesia), and Siegen (Westphalia); in Russia at Daschkesan (Caucasus), at the latter place it occurs in felsite porphyry and is free from nickel.

Earthy cobalt, *asbolan* or *wad*, is a mixture of varying quantities of cobaltous oxide, with manganese peroxide, and ferric hydrate. The proportion of cobalt varies from 2 to 20 per cent. It occurs in small quantities on the outcrop of cobalt ore deposits. Extensive deposits of it have been discovered in New Caledonia, and contain from 3 to 5 per cent. of cobalt. It also occurs at Asturias in Spain, and there contains 15 per cent. of the metal.

Other cobalt minerals which deserve mention, although, on account of their comparative rarity, they do not form the basis for a separate process of extraction, are:—*Linnæite*, Co_3S_4, which often contains more nickel than cobalt and is then known by the name *cobalt nickel pyrites*; it occurs in Sweden; at Müssen near Siegen; at the Motte mine in the State of Missouri:—*cobalt bloom* or *erythrine*, $Co_3As_2O_8+8H_2O$, which occurs in the outcrop of cobalt ore deposits, usually those of arsenical ores; it is found at Schneeberg, Saalfeld, Riechelsdorf, Siegen, Cornwall and Cumberland:—*cobalt vitriol* or *bieberite*, $CoSO_4+7H_2O$, which occurs at Bieber in Hesse. Cobalt ores are nearly always found with nickel ores; the metal is found with nickel and iron in meteorites.

METALLURGICAL PRODUCTS CONTAINING COBALT WHICH ARE USED AS SOURCES OF SMALT AND COBALT MATTE

These are matte, speiss and slag. The cobalt which exists in small quantities in a great variety of ores, especially in those of nickel, is collected into speiss or matte, and has to be extracted from these in the metallic form. The amount of cobalt in the matte or speiss is always very small. Cobalt is also found in slags from matte containing cobalt and nickel, when these are treated by oxidation processes.

THE EXTRACTION OF COBALT AND COBALT COMPOUNDS

Metallic cobalt has had a very limited technical application up to the present time, and is produced only in small quantities and by methods exactly similar to those in use for the production of nickel, viz., by the reduction of cobaltous oxide CoO, or cobaltic oxide, Co_2O_3. Cobalt ores, however, are used in very large quantities for the production of *smalt*, a silicate of cobaltous oxide and alkalies, which possesses an intense blue colour, and is used as a pigment. (Silicate of cobalt itself is an exceedingly strong colouring agent, surpassed only by gold. A proportion of one-tenth per cent. in glass gives it a deep blue colour.) Other cobalt pigments are produced in smaller quantities; such are the phosphate, the arseniate (known as *red oxide of cobalt*), *cobalt bronze*, which is a double phosphate of cobalt and ammonium, *cobalt ultramarine*, or *Thenard's blue*, which is an intimate molecular mixture of alumina with different oxides of cobalt, *Rinmann's green*, and others.

Up to the present time metallic cobalt has been prepared only by wet methods. The metal is precipitated from solution as the sesquioxide Co_2O_3, which is afterwards reduced by charcoal. The production of the metal entirely by dry methods has not yet proved practicable on account of the impurities of the ores or metallurgical products employed. Nor does it appear that any one has yet produced it in compact form by electrolytic means, although electrolytic coatings of the metal have been obtained on other metals and alloys. All that has been said before about the electro-metallurgy of nickel applies equally to cobalt.

For the reasons given above the extraction of cobalt is more frequently carried on in chemical works than in smelting houses, and the methods employed are largely kept secret, as in the case of nickel.

A dry direct process for the treatment of rich cobalt ores is used for the production of smalt, and also to a smaller extent for the preparation of cobalt arseniate. Other cobalt compounds are prepared in chemical works from cobaltic oxide or from salts of cobalt by means of wet methods.

We therefore have to distinguish:—

(1) The extraction of cobalt oxide, Co_2O_3, and metallic cobalt.

(2) The production of smalt.

1. THE EXTRACTION OF COBALT OXIDE AND METALLIC COBALT

A. THE EXTRACTION OF COBALT OXIDE

Pure cobalt oxide in quantity has as yet been prepared only by wet methods, either from ores or from furnace products. The oxide resulting from roasting ore, speiss or matte which contains sulphur or arsenic, or both, is always too impure, and requires to be dissolved in order to remove impurities and to obtain a pure product. It has been proposed[1] to produce from sulphuretted ores a matte free from iron, and containing only sulphur and nickel besides the cobalt: this matte was to be fused under a blast on a bed of quartz and sodium silicate in order to produce a silicate of cobalt, and this latter was to be fused with soda and nitre in order to liberate the cobalt oxide. The method, however, does not appear to have come into use.

The common methods for producing cobalt oxide from ores which but rarely contain any ingredients beside nickel, iron and (principally) copper, in addition to the cobalt, has already been described under nickel, for the wet methods for the extraction of nickel are usually preceded by a separation of cobalt in the form of sesquioxide. These will accordingly be found under nickel.

The compounds containing sulphur, arsenic, sulpharsenides, &c., are first dead roasted in order to drive off sulphur and arsenic and convert the heavy metals into oxides. The same object may be attained by the more costly method of smelting the unroasted ore with soda and saltpetre, or with sulphur and soda-ash, or potash; in this case arseniates and sulpharseniates, or sulphates of the alkali are formed, and may be removed by lixiviation, the heavy oxides being left behind.

The oxides so obtained, or the ores where these already contain the metals as oxide, are treated with hydrochloric or sulphuric acids, which dissolve the cobalt, nickel, iron, copper, and other soluble oxides. Lead, copper and bismuth are precipitated from the solution thus obtained by sulphuretted hydrogen or an alkaline sulphide, and the solution, when separated from the precipitated sulphides, is treated with the exact quantity of chloride of lime necessary to convert the ferrous into ferric oxide, which latter is then thrown down by the addition of powdered chalk.

(The bismuth could be thrown down from the hydrochloric acid solution by the addition of water, in the form of basic chloride, instead of being precipitated with the lead, copper, &c., by means of sulphuretted hydrogen.)

The cobalt is precipitated from the liquid, after the iron has been removed, by the cautious addition of chloride of lime to the warmed solution. It is thrown down as sesquioxide, and unless care is taken to avoid excess some nickel comes down with it. The solution which remains after the cobalt has been separated yields nickel when treated as before described. Cobalt may also be precipitated after the nickel. In this case soda is added to the boiling solution, which precipitates nickel monoxide with a small amount of cobalt monoxide, while cobalt with a trifling quantity of nickel remains dissolved. It may now be precipitated as sesquioxide by adding more soda, or by chloride of lime.

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[1] Muspratt-Kerl, *Handb. der Techn. Chem.*, 3rd ed., vol. iii., p. 1938. *Graham-Otto, Chemistry*, 1889, p. 915.

Another method for the separation of cobalt and nickel consists in first neutralising the concentrated solution with potash lye, then making it faintly acid with acetic acid, and treating it with potassium nitrite, which throws down cobalt as cobaltic-potassium nitrite, nickel remaining in solution. When the precipitate is ignited it is converted into cobalt sesquioxide. If lime is present, potassium nitrite is of no use for separation, for Erdmann finds that in that case a salt of nickel and calcium is also precipitated ($K_2CaNi(NO_2)_6$). Other alkaline salts have also been proposed for the purpose.

Patera formerly employed bisulphate of potash, which throws down nickel completely as a difficultly soluble double salt containing a small quantity of the cobalt compound.

According to Kunzel, bisulphate of ammonia is more suitable. The latter precipitates the nickel double salt when the solution is sufficiently concentrated, while the cobalt compound remains in solution. From this solution cobalt is precipitated as sulphide by ammonium sulphide, and this converted into sesquioxide by roasting.

As instances of the recovery of the sesquioxide from smelting products containing nickel and cobalt, we may take the process at the Scopello Works, already described under nickel (p. 581), and at the George Works at Dobschau (p. 586); and also the method at the Editha Smalt Works in Silesia, and at similar works at Oberschlema in Saxony.

Lundborg[1] describes the treatment at the Editha Smalt Works of ores containing earthy cobalt, with concentrated hydrochloric acid in clay vessels, steam being blown through. Iron is first thrown down from the solution by adding separate small portions of marble and keeping at a certain temperature. As soon as nickel begins to come down, the separation of iron is known to be complete.

Soda is now added to the filtrate to precipitate nickel. When cobalt begins to come down, the liquid is filtered, and precipitation continued, a mixture of the two monoxides now falling until all the nickel has separated. Lastly, pure cobalt monoxide may be thrown down from the final filtrate. The precipitate of mixed oxides is accumulated and redissolved, and the two separated similarly by fractional precipitation.

The matte from the Sesia Works at Oberschlema, in Saxony, is similarly treated. It contains 16 per cent. Ni, 14 per cent. Co, 50 per cent. Cu, and 20 per cent. S. The powdered matte is roasted in a reverberatory furnace and treated with dilute sulphuric acid. The copper is first precipitated by iron, after which the remainder of the process is the same as that described above. Extraction of cobalt from roasted ores and smelting products, or from oxidised ores, by means of mineral acids, may be carried on if there are not many other substances present which will dissolve in the acid; it is especially important that the ores do not contain too much soluble gangue; otherwise, with a rather poor material originally, the successive filtrates will be so impure and contain so little cobalt that it will be barely, or not at all, worth while to work them up into the sesquioxide. For the working of such mixtures methods have been proposed by Herrenschmidt and Stahl, which will now be shortly described.

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[1] *Jern. Cont. Annalen*, 1876, pt. 2.; *Berg. und Hütt. Ztg.*, 1877, p. 35.

Herrenschmidt's[1] method, already described under wet methods for nickel, is used at the Malétra Co.'s works at Petit Querilly, near Rouen; it has for its object the working up of oxidised cobalt ores, and especially one from New Caledonia, an *asbolan*, containing nickel, manganese and iron, mingled with clay. The average composition of this ore is:—[2]

MnO	18	per cent.
CoO	3	"
NiO	1·25	"
SiO_2	8	,
Fe_2O_3	30	"
Al_2O_3	5	"
CaO	1	"
MgO	1	"
Loss by ignition	32·75	"

The finely powdered ore is treated with ferrous sulphate solution, which deposits ferric oxide and brings cobalt, nickel and manganese into solution as sulphates. To facilitate solution the whole is agitated by a current of steam. (The green vitriol solution is made in the works by acting on cuttings of iron with sodium bisulphate solution and separating ferrous from sodium sulphate by crystallisation.)

The solution containing the three sulphates is separated from the residue by a filter press, and treated with sodium sulphide in precipitation vats, whereby the whole of the cobalt and nickel and a small portion of the manganese are precipitated.

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[1] *Genie civil*, 1891, 18, 373; *Monit. Scientif.* vol. vi., May, 1892; *Berg. und Hütt. Ztg.*, 1892, p. 464; 1893, p. 1.

[2] *Berg. und Hütt. Ztg.*, 1892, p. 464.

(The sodium sulphide is made in the works by treating the black residues of the Leblanc soda process with sodium sulphate and water and warming, when by double decomposition calcium sulphate separates and a solution of sodium sulphide is obtained.)

The precipitate of metallic sulphides is separated by a filter press, and treated with solution of ferric chloride, which decomposes and dissolves manganese sulphide but does not act on the other two. A fairly pure residue of nickel and cobalt sulphides is thus obtained, and a liquid containing manganic sulphate and manganous chloride with ferric and ferrous sulphates and chlorides. This liquid after being separated may be treated with excess of chalk, and air blown through, which gives a precipitate of calcium manganite, that can be worked up with the Weldon mud in the manufacture of chlorine.

The two sulphides thus freed from manganese are dried and subjected to a careful roasting to convert them into sulphates. The latter are washed out by hot water, and treated with calcium chloride which forms their soluble chlorides, precipitating calcium sulphate. The filtered liquid has to be freed from the small amount of iron in it by copper oxide, and this copper thrown down by nickel monoxide. Then it is divided into two parts. From one cobalt and nickel are thrown down by lime as hydrates, the precipitate carefully washed and suspended in water, then treated with chlorine gas and air, which convert both hydrates into sesquioxides. The nickel sesquioxide so formed is now used to precipitate cobalt from the other half of the solution. For this purpose the precipitate of sesquioxides is added to the solution of the two chlorides and stirred about with the assistance of a current of steam. Nickel sesquioxide is reduced to monoxide and passes into solution, and the equivalent in cobalt sesquioxide is precipitated, with the original, which is not dissolved at all.

The whole cobalt is now precipitated as sesquioxide, the whole nickel dissolved as chloride. The latter may be thrown down from the liquid as monoxide by milk of lime.

The cobalt sesquioxide is washed, pressed, dried, and ignited.

When the nickel is precipitated the calcium chloride produced can be used in the process to act upon the sulphates (formed from sulphides by roasting).

Nothing is known yet as to the economic results of this method. It seems to be most suitable to a Leblanc soda works, where chlorine is made by the Weldon process.

Stahl's[1] method consists in a chlorinating of ores poor in cobalt with waste products and pyrites so as to form cobalt chloride; then the soluble salts are washed out of the product, cobalt precipitated from the liquid as sulphide, and this converted into oxide. Stahl discovered that a chlorinating roasting completely acted on nickel and cobalt, giving chlorides, and on manganese to a great extent, while iron became oxidised; (if the wash water is slightly acid it is impossible to prevent a little iron being dissolved). Any soluble alkaline earths in the ores are converted into sulphates by the roasting. Calcium and magnesium sulphate pass into the solution with the chlorides of cobalt, nickel, copper and manganese, and also freshly formed alkaline sulphates and undecomposed alkaline chlorides. (Calcium sulphate will be to a great extent thrown down by evaporating the wash liquor to a certain density.)

Stahl treats the liquor in the following way. First copper sulphide is thrown down by sulphuretted hydrogen, and filtered off. The liquid is neutralised by soda, and sodium sulphide added to precipitate sulphides of cobalt, nickel, iron, manganese and any copper remaining. Manganese is the last to come down, and so may be nearly all left in the solution by carefully regulating the amount of the precipitant.

To separate cobalt sulphide from the others, Stahl[2] treats them with a mixture of acetic and sulphurous acids until the reaction is slightly acid. Sulphurous acid decomposes any sulphuretted hydrogen produced and prevents its being noxious. The residue is separated by a filter press, roasted to convert the sulphides into oxides, and then treated with hot pure soda lye to decompose any sulphates remaining; finally it is washed, dried, and ignited.

Stahl tried this method on an ore of this composition:—

Co	1·02 per cent.	Fe_2O_3	5·56 per cent.
Ni	Trace	Al_2O_3 P_2O_5	1·06 „
As	2·46 „	CaO MgO	0·81 ,
Cu Fe S_2	0·53 „	Insoluble residue	88·36 „

The ore was ground down to about 0·06 inch mesh, and placed in a long-bedded calciner; it was alternately oxidised and reduced during roasting to get rid of arsenic. Reducing was effected by adding sawdust. The result, free from arsenic, was subjected to chlorinating roasting in a special furnace (most likely a muffle furnace). For this purpose it was mixed with 15 per cent. of its weight of *abraumsalz*[1] (which is 95 per cent. alkaline chloride) and 10 per cent. of its weight of pyrites free from zinc and nickel; then it was roasted at a red heat until the cobalt is fully chlorinated. Stahl gives the following reactions:—

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[1] *Berg. und Hutt. Ztg.*, 1893, p. 2.; German patent, No. 58,417.

[2] Additional patent, No. 66,265.

1. $$8FeS_2 + 22O_2 = 4Fe_2O_3 + 16SO_2.$$

2. $$\left\{\begin{array}{c} 12NaCl + 6SO_2 + 3O_2 + 6H_2O = 6Na_2SO_4 + 12HCl; \\ 2Co_3O_4 + 12HCl = 6CoCl_2 + 6H_2O + O_2. \end{array}\right.$$

3. $$Co_3O_4 + 6NaCl + 3So_2 + O_2 = 3CoCl_2 + 3Na_2SO_4.$$

4. $$\left\{\begin{array}{c} 6SO_2 + 3O_2 = 6SO_3; \\ 2Co_3O_4 + 12NaCl + 6SO_3 = 6CoCl_2 + 6Na_2SO_4 + O_2; \end{array}\right.$$

and so on.

The product was washed, in lixiviating vats fitted with straw filters, four times with slightly acid water and then with pure water. This acid water was obtained by leading the gases from the roasting into condensation towers, where the acid portiôn was absorbed by water. The wash liquor contained 0·41 per cent. Co and Ni, 0·075 Cu, traces of iron and manganese, and small quantities of sodium chloride, calcium and magnesium sulphates, and appreciable quantities of alkaline sulphates. The residue after washing contained 0·04 per cent. Co and Ni. Another ore containing 1·08 Co was similarly treated and gave a liquor containing 0·429 per cent. Co, 0·006 per cent. Fe, 0·031 Mn, 0·004 Cu; and small quantities of salts just as above. The residue contained 0·07 per cent. Co.

Another ore of which the composition was:—

Co	1·49 per cent.	Al_2O_3 P_2O_5	2·52 per cent.
Ni	0·02 ,,		
As	4·09 ,,	Mn_2O_3	1·44 ,,
Cu Fe S_2	Trace	CaO MgO	0·36 ,,
		Alkali	Trace
FeS_2	1·35 ,,	Insoluble residue	74·96 ,,
Fe_2O_3	14·02 ,,		

produced a liquor with 0 643 per cent. Co and Ni, 0·057 per cent. Fe, 0·296 Mn. The residue contained 0·09 per cent. Co and Ni, 0·21 per cent. As, 21·10 per cent. Fe_2O_3, and 0·42 per cent. Mn_2O_3.

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[1] *See* Vol. I., p. 10.

Ores with 2·81 per cent. Co, 0·04 per cent. Ni, and 7·29 per cent. As were treated in the same way, and left residues with 0·11 per cent. Co and Ni, and 0·27 per cent. As.

By treatment of these liquors in the way described Stahl obtained an oxidised product with 92 per cent. Co_2O_3.

Whether this method was ever worked is not known to the author. It seems possible that, if the cost of reagents is low, poor ores containing about 1 per cent. cobalt can be worked by it with profit.

According to another method[1] the dead roasted ore is re-roasted with chlorides of iron, whereby cobalt chloride is formed with ferric oxide and ferroso-ferric oxide:—

$$(Co_3O_4+3FeCl_2=3CoCl_2+Fe_3O_4;$$
$$2Co_3O_4+2Fe_2Cl_6=6CoCl_2+Fe_2O_3+O_2).$$

As far as the writer knows, no experiments have been yet made on a large scale to ascertain whether the conversion of cobalt into chloride is complete.

Sack[2] has patented a process for separating cobalt from manganese, iron and aluminium, based on his researches on lead peroxide and its hydrate. He found that when a liquid containing 0·308 per cent. Co and 0·4156 per cent. Mn was treated with lead peroxide at ordinary temperatures, the resulting liquid contained 0·3638 per cent. Co and 0·00076 per cent. Mn. The two metals were present as sulphates. Further he found that manganese peroxide would precipitate aluminium. Iron, he showed, was thrown down as basic salt.

The liquid (preferably a solution of sulphates) is first freed from any copper it contains, and then well mixed with the calculated quantity of peroxide of lead. In case iron is present in great quantity it is precipitated beforehand with an alkaline (or alkaline earth) carbonate, and a large proportion of manganese, if present, is got rid of by fractional precipitation with a soluble alkaline or alkaline earthy sulphide.

The precipitate produced by lead peroxide, which consists of hydrated peroxide of manganese, alumina, basic ferric sulphate and lead sulphate, is to be brought into solution (all but the lead) by sulphuric or hydrochloric acid, and the residue of lead sulphate worked up again into peroxide. This method does not appear to have been used on the large scale.

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[1] Schoneis, *Berg. und Hütt. Ztg.*, 1890, p. 453; *Chemiker Ztg.*, 1890, p. 1475; *Zeitschr. f. Angew. Chemie*, 1890, p. 337.

[2] German patent, Kl. 40, No. 72,579, Aug. 5, 1892.

Lastly, there should be mentioned a proposal by Vortmann[1] to obtain cobaltic oxide or hydrate from solutions containing cobalt and nickel, by electrolysis. If a current is passed through solutions of these metals containing no alkaline sulphates or other neutral salts of the alkalies, cobaltous and nickelous hydrates or basic salts of both come down at the cathode. If the current is reversed the nickelous hydrate (or corresponding basic salt) dissolves, but not that of cobalt, which is oxidised to cobaltic hydrate instead. On restoring the current to its original direction more of each lower hydrate is produced, and on again reversing the current the nickel is dissolved. In this way, finally, all the cobalt is precipitated as hydrate and all the nickel remains in solution. If there is a small quantity of a chloride present in the liquid (say 1 per cent. common salt), the cobaltous hydrate is very quickly oxidised to the higher compound by the small amount of free chlorine or hypochlorous acid set free. In this case the constant change of current is unnecessary.

The separation of cobalt is assisted by gentle warming. After it is completed, the current is stopped and the liquid heated to 60° or 70°, whereby any small quantity of nickelic hydrate remaining in the cobalt compound is dissolved away. The solution of nickel when filtered contains no cobalt. Nothing is known yet as to the use of this proposal on the large scale.

Clemens Winkler[2] has given an account of his method of obtaining pure cobalt and pure nickel in determining their atomic weights.

B. THE EXTRACTION OF METALLIC COBALT

This is achieved by the reduction of the sesquioxide with carbonaceous bodies and is carried on exactly in the same way as the reduction of nickel from its monoxide.[3]

The melted cobalt, free from carbon, can be cast into plates, which may be rolled when hot. The addition of a trace of magnesium (0·1 per cent) assists the production of a compact and tenacious casting.

A patent[4] is in use at the Berndorf works in Lower Austria for the production of cobalt which is malleable and can be forged. The oxide is used in the form of powder; it is mixed with a 4 per cent. solution of alkaline permanganate, dried and smelted in a blast furnace, which gives cobalt containing a trace of manganese. The manganese compound renders the gaseous carbon compounds innocuous by oxidising them. (Carbon, which is taken up by cobalt to the extent of 4 per cent., makes it hard and brittle.)

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[1] German patent, No. 78,236, May 10, 1894.

[2] *Zeitschr. fur Inorg. Chemie*, vol. viii., 1895.

[3] See p. 551.

[4] German patent, No. 28,989.

2. THE PRODUCTION OF SMALT

Smalt is a potash glass highly silicated and coloured blue by cobalt monoxide. Various qualities, classified according to shade and fineness of grain, are found in commerce. It contains usually a certain quantity of water-glass and also minute quantities of arsenic or arsenious acid. According to Ludwig[1] the colour may be injured in purity and strength by the presence of certain metallic oxides. According to his researches baryta deepens the colour somewhat, but gives it an indigo-blue tinge. Soda, lime, and magnesia diminish the colour in a marked degree, and give it a reddish shade. Alumina does not affect the purity of the colour, but diminishes its intensity. Nickel monoxide gives the glass a red colour if it is in small quantities; a large amount gives a violet-brown tint; ferrous oxide gives a shade varying from brown to green. Manganic oxide gives violet, cupric oxide green, cuprous oxide red shades. Ferric oxide, manganous oxide, lead and bismuth oxides are harmless if not in too great quantities. The quantity of cobalt in the smalt varies with its depth of colour from 1·95 to 18 per cent.

Smalt is manufactured by melting together in proper proportions cobaltic oxide, quartz and potash.

The oxide is generally made direct from the ores by roasting, unless it is made by a wet method. If the ores to be roasted contain arsenical or sulph-arsenical compounds of cobalt, the roasting furnaces (reverberatory or muffle furnaces) must be provided with condensers to arrest the arsenious acid set free.

The roasting should be carried on so that the cobalt in the ore is converted into sesquioxide. If a considerable amount of iron or nickel is present, a certain amount of metallic arsenide is purposely left undecomposed to separate those metals in a speiss during the smelting process. But if the roasting is terminated too soon, cobalt will remain combined with arsenic, and pass into the speiss. A small quantity thus lost need not be regretted as it ensures the absence of nickel in the smalt. If iron is in the ore there is also advantage in keeping back a little arsenious acid in the roasted product, as during the smelting this will convert ferrous oxide into the much less injurious ferric oxide.

Silica is used in the form of pure ground quartz. To obtain this lumps of quartz are ignited, dropped into water so as to render them brittle, and then stamped. The pulverised quartz is finally washed to get rid of any foreign matter.

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[1] *Erdmann's Journ. fur Pract. Chem.*, vol. li., p. 129.

The potash must be pure and calcined, and must be free from soda and alkaline earths.

The ore, the quartz and the potash are most intimately mixed in accurate proportions, either ascertained by experience or discovered by preliminary trials, and then put in the melting crucible of the smalt furnace. If there is not arsenious acid enough in the ore to oxidise the ferrous oxide, the requisite amount is added to the charge.

The smelting crucible or pot is made of fire-clay, and varies in size in different works.

At the Saxony smalt works a pot holds about 1 cwt. of the mixture, and there are 8 pots in a furnace.

The arrangement of a furnace for 6 pots is shown in Figs. 339 and 340.

On the bottom of the dome-shaped heating chamber *T*, the pots *t*, *t*, are placed on tiles round an opening *z*, through which the flame ascends from the two hearths *E*, *E*, below. The smoke and gases, after circulating round the pots, pass away through the openings *m*, *m*, which are also working doors. The pots are put in and taken out through the openings *v*, which are bricked up during heating. *N* is the ashpit, *H* the floor level of the works.

During the fusion cobalt sesquioxide, silica and the potassium of the potash unite into a glass, the smalt, while nickel, iron and copper unite with the arsenic into a speiss. Bismuth, if present, separates with the speiss. If copper is present as oxide, it yields its oxygen to the readily oxidisable metals, and is also found in the speiss.

The speiss and any bismuth present are found at the bottom of the pot, the cobalt glass above. While fusing, the mass is stirred up from time to time. Finally the molten mass is allowed to stand quiet for a while for the two layers to separate completely. Then the glass is lifted out with a ladle, and poured into cold water, to be ready for powdering.

The length of the operation varies from 8 to 16 hours according to the charge and the quality of the glass to be obtained.

On account of the purity of the speiss it is a suitable material for the recovery of nickel. If the ore contains bismuth, large quantities of this metal are mixed with the speiss. It is obtained by liquation before working up for nickel.

After being thrown into water, the glass is stamped, sieved jigged to free it from any intermixed speiss, and then ground wet in mills. The mud is sent through a series of washing vats in which the glass powder is deposited according to the size of its granules. In the first is the coarse powder, called "*streublau*."

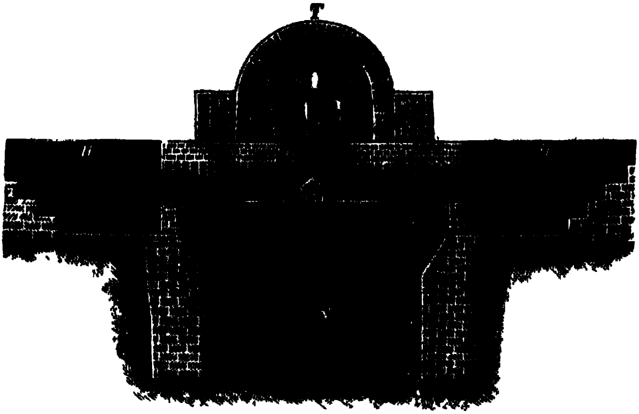

Fig. 839

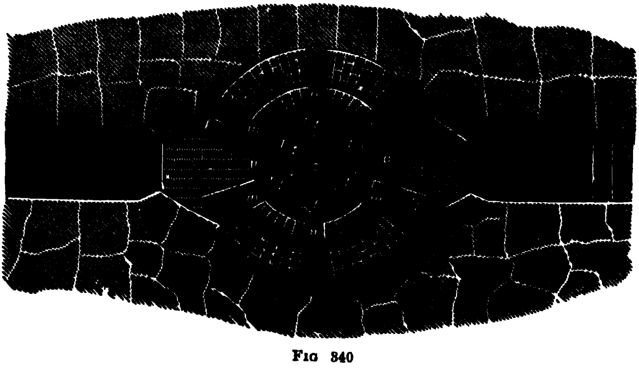

Fig 840

This is ground again with glass of the same depth of colour. After this is removed, the mud is run into a second wash vessel, in which the pigment proper is deposited. Next, the liquid still containing suspended particles, is run into a third vessel, where it stands till clear. At the bottom of this the finest powder is found, the so-called "*eschel*." The pigment and the *eschel* are washed several times, and the wash-water collected in a tank in which the so-called "tank-eschel" is deposited.

The pigment is now put into hot drying chambers, or dried in the open air in the "drying-houses."

It is only known as smalt after this drying process. During all this treatment it has lost some part of any soluble constituents, but from 0·75 to 1·25 per cent. of water-glass remains. It has a dull appearance if the percentage approaches the higher limit. It forms a plastic mass when mixed with water. If left in contact with water too long it loses its fine colour and becomes grey-blue or dirty green.

Smalt is classified by the size of the grains, as well as by its content of cobalt. Letters are used to distinguish both the qualities:—

Classification by size

C (colour, pigment).
E (eschel).
B (Bohemian, *i.e.*, of medium coarseness from 0·02 to 0·04 inch diam).
H (high, *i.e.* largest size).
S is used to distinguish unsieved pigment.
G is used to distinguish sieved pigment.

Classification by content of Cobalt

F (fine).
M (medium).
O (ordinary).

These letters are combined to distinguish quality: the following examples of their use:—

FC = Fine colour. FCB = Fine Bohemian colour. ME = medium eschel. OCB = ordinary Bohemian colour. Smalts which contain more cobalt than the F quality are distinguished by doubling the letter F, and qualities poorer in cobalt than the OC quality are distinguished by the use of indices, e.g. OC^2 (i.e. containing half the cobalt in the OC quality); OC^4 (i.e. containing a quarter of that quantity).

Ludwig has given the following analysis of smalts; (1) a coarse colour from Modum, (2) a German coarse eschel, and (3) a German coarse pale colour.

	I.	II.	III
SiO_2	70·86	66·20	72·12
Al_2O_3	0·43	0·64	1·80
FeO	0·24	1·36	1·40
CaO	—	—	1·92
CoO	6·49	6·75	1·95
K_2O	21·41	16·31	20·04
Ni	—	—	trace.
As_2O_3	trace		0·078
CO_2	—	0·25	0·46
H_2O	0·57	0·67	trace

By *zaffre* or *safflor* is understood a mixture of roasted cobalt ore and powdered quartz, which when melted with potash will yield blue glass. This is also an article of commerce.

3. THE MANUFACTURE OF SPECIAL COBALT COMPOUNDS

Amongst these may be noticed :—

Cobalt phosphate and arseniate, which are known in commerce as *red oxide of cobalt*; *cobalt bronze*, a cobalt-ammonium phosphate which produces a metallic tinsel; *cobalt-ultramarine* or *Thenard's blue*, which is a molecular mixture of alumina and an oxide of cobalt and *zinc green*, or *Rinmann's green*, or *green cinnabar*, a compound of zinc and cobaltous oxide

Cobalt-ultramarine is made by treating a solution containing 3 parts alumina and 1 part cobalt monoxide with an alkaline carbonate; or by igniting a mixture of alum and cobalt sulphate until the whole of the sulphuric acid has been got rid of. It may also be obtained by treating solution of cobalt nitrate with potassium phosphate, collecting the precipitate, mixing it with three times its volume of aluminium hydrate (freshly precipitated by sodium carbonate from alum solution) and heating and drying this mixture.

Rinmann's green may be made by treating a solution of 1 part cobaltous chloride and 5 parts zinc chloride with potassium carbonate, washing, drying and igniting the precipitate obtained. Another method consists in igniting a mixture of blue cobalt chloride with zinc white until no more zinc chloride volatilises. Another is to treat a solution of zinc and cobalt sulphates with sodium carbonate, wash and ignite the precipitate. It is also prepared by evaporating to dryness a solution of zinc and cobalt nitrates and igniting the residue. Or lastly, by mixing cobalt nitrate solution with zinc oxide, evaporating to dryness, and igniting the residue.

In all these cases the colour may be spoiled, and turned grey by allowing the temperature to rise too high during ignition.

PLATINUM

PHYSICAL PROPERTIES

PLATINUM has an almost silver-white lustre and a hackly fracture. It is ductile and malleable [illegible] a very high degree. Its hardness is equal to that of copper: its tenacity lies between those of gold and copper.

Its specific gravity is, according to Deville and Debray, from 21·48 to 21·50 at 17·6° C.; by the addition of a certain quantity of iridium it rises to 21·8. It crystallises in the regular system. It can be welded at a white heat, and melts in the oxy-hydrogen jet at about 1775° (Violle), or according to earlier statements at about 2000°. If combined with carbon and silicon it will melt at a lower temperature.

The question of the volatility of platinum at higher temperatures has not yet been decided with certainty. It is well known that when quite pure it may be heated far above its melting point in the oxy-hydrogen blast, without any loss whatever by volatilisation. But it has been proved to be volatile when combined with silicon or carbon. Further, it is volatile in the presence of chlorine and osmium.

If quickly cooled, molten platinum is said to spit in the same way as silver. According to Heræus the spitting occurs only when oxygen is forced into the molten metal. According to Aubel the cause of the spitting is that the surface of the metal is contracted by a quick cooling, and the liquid portions underneath are forced out and burst through this cover.

At a high temperature platinum is permeable by hydrogen. Under the same conditions oxygen, chlorine, hydrochloric acid, carbon monoxide and dioxide, and steam will not pass through. It is permeable by nitrogen in small quantities, but only in the presence of hydrogen. The red-hot metal has the property of absorbing considerable quantities of hydrogen, and of retaining it on being cooled. The hydrogen is removed by heating the metal in a vacuum.

Finely divided platinum (platinum black, spongy platinum) has the property of condensing gases, especially oxygen, on its surface.

Its ductility is considerably lessened by the presence of small quantities of the other platinum metals (which are found with it in nature), such as iridium, osmium, palladium, rhodium, ruthenium. On the other hand iridium makes platinum harder, and less easily attacked by chemical agents. Silicon even in very small quantity (one three-thousandth part) makes platinum brittle and hard.

CHEMICAL REACTIONS OF PLATINUM AND OF ITS COMPOUNDS THAT ARE OF IMPORTANCE IN ITS EXTRACTION

Platinum is unalterable in air at all temperatures. In the pure state it is not attacked by sulphuric, nitric or hydrochloric acid, cold or hot. But if it is impure or alloyed with other metals, it will be more or less acted on by acids. For instance, from its alloys containing silver, copper, lead, bismuth and zinc it dissolves in nitric acid, forming platinic nitrate. Platinum is slowly dissolved by aqua regia to form platinic chloride, and much more quickly under increased pressure.

Perfectly dry chlorine does affect platinum at the ordinary temperature, but acts readily at a higher temperature. Platinum sponge is converted into the lower chloride at about 250°C. Damp chlorine, like aqua regia, acts on it slowly at ordinary temperatures, rapidly at higher temperatures. Ferric chloride seems to dissolve platinum. There are two chlorides, platinous chloride, $PtCl_2$ and platinic chloride, $PtCl_4$. Bromine does not attack it: but a mixture of bromine or hydrobromic acid with nitric acid acts readily.

It is oxidised by fused alkali, in the presence of air, and also by heating with alkaline nitrates. There are two oxides, PtO and PtO_2.

When sulphur is heated with finely divided platinum in a glass tube in a vacuum, the two substances combine readily to form the monosulphide PtS. If heated to redness in the air this compound decomposes, and platinum metal remains. Another sulphide, platinum disulphide, PtS_2, is obtained by melting platinum with sulphur and an alkali, or by melting the double chloride of platinum and ammonium with sulphur. This disulphide dissolves in alkaline sulphides.

Silicon combines with platinum if the latter is heated with carbon and silica, or if heated with carbon alone in a clay crucible. By melting platinum with silicon, Winkler obtained the compounds $PtSi_3$ and Pt_2Si. They are brittle and hard, and lose their silicon at very high temperatures.

Platinum combines with phosphorus at a red heat.

Metallic platinum is deposited from all its salts when they are heated to redness. If a solution of the chloride is treated with organic substances such as alcohol, or with magnesium, zinc or iron, platinum separates in the form of a black powder known as platinum black.

Potassium and ammonium chlorides give with a solution of platinum chloride precipitates of the respective double chlorides. When these are heated, metallic platinum is left in a spongy form. If it is the potassium-platinum chloride that is heated, potassium chloride is left behind as well as the metal.

Platinum alloys with a large number of metals; for instance, with iridium, osmium, palladium, rhodium, ruthenium, gold, silver, copper, iron, lead.

Compact platinum does not amalgamate with mercury in the cold. When heated it forms a slight coating of amalgam which is easily wiped off. However, spongy platinum takes up mercury when the two are rubbed together and gently warmed with the addition of slightly acidified water.

Since the platinum found in nature is compact, it can be separated by mercury from native gold.

If platinum is melted with lead a brittle alloy is obtained, from which lead may be driven off by cupellation. If the alloy is powdered and exposed to moist air containing carbon dioxide, the excess of lead will be oxidised away as white lead, until just enough is left for the alloy Pt+Pb, which remains. This is easily decomposed by heating with mineral acids. Thus it is possible to collect platinum by melting it in lead, and then removing the lead by cupelling.

ORES OF PLATINUM

Platinum is found in the native condition, and combined with arsenic, as the mineral *sperrylit*. Only native platinum is used as a source of the metal. *Sperrylit* occurs in the copper and nickel ores of Sudbury, in Canada, which contain veins of magnetic pyrites; it seems to have the formula $PtAs_2$, and has only mineralogical interest.

Native platinum is usually alloyed with the metals known as the platinum group, namely, iridium, osmium, rhodium, palladium, ruthenium, and also with iron and some copper. As much as 27·8 per cent. of iridium has been found in specimens of platinum, and 19 per cent. of iron.

Platinum is found most usually in beds of gravel and sand which have been formed by the wearing away of the original deposits containing the metal. In such secondary deposits known as "alluvials" or "placers," it is found like gold in grains and flakes, more rarely in nuggets. The chief impurities are serpentine, quartz, zircon, spinel, corundum, titanic, chrome, and magnetic iron ores, gold, and osmiridium. The largest lump of platinum found up till now in the "alluvials" of the Ural Mountains is in the Demidoff Museum at St. Petersburg, and weighs 21·64 lbs.

The most important sources of native platinum are in Russia; which country produces far more of this metal than any other. Platinum is found there both on the eastern and western slopes of the Urals, and also in the Altai Mountains. The richest part of the Urals, whence the greatest share of the Russian output comes, is Nischni-Tagilsk on the west side. On the eastern side platinum is found at Bogolovsk, Kuschvinsk, Nevjansk and Miask. Other localities for platinum are Spain, Ireland (co Wicklow), South America (the provinces Choco and Barbacoas in the Republic of New Granada, Minas Geraes, and Matto Grosse in Brazil), North America (British Columbia, California, Oregon, North Carolina, Canada, Mexico, San Domingo, Hayti), Borneo, East Indies, Lapland, Australia (New South Wales), New Zealand. Platinum to the extent of 0·0004 per cent. has been found in the sand of the Rhine by Hopff and Döbereiner.

The alluvial soil or sand containing platinum is washed, and any gold present in the residue removed by treatment with mercury. In this condition it is sent to the platinum works for further treatment.

The composition of the platinum thus obtained, the so-called crude platinum, will be seen in the following analyses:—

	Russian Platinum						Platinum from British Columbia Analysed by Hoffmann		California	Brazil	Choco	Borneo
	from Nischni Tagilsk in the Urals Analysed by Kern[1]				from Goroblagodat in the Urals Analysed by Kern[2]				Deville	Svanberg	Deville and Debray	Blekerode
	I.	II.	III.	IV.	V.	VI.	VII.	VIII	IX.	X.	XI	XII.
Pt	80·87	71·20	89·05	87·50	84·50	80·05	78·43	68·19	79·85	55·44	86·20	70·21
Ir	0·06	2·40	tr.	0·05	0·90	2·50	1·04	1·21	4·20	27·79	0·85	6·13
Os	tr.	0·05	tr.	0·01	0·06	tr.	—	-	0·05	—	—	1·15
Pd	1·30	1·95	2·35	1·05	0·05	2·03	0·09	0·26	1·95	0·49	0·50	1·41
Rh	4·44	1·50	4·60	1·20	2·90	1·05	1·70		0·65	6·86	—	0·50
Fe	10·82	13·40	3·40	8·60	7·55	11·04	9·78	7.87	4·45	4·14	7·80	5·80
Cu	2·30	6·70	0·59	0·65	0·60	1·02	3·89	3·09	0·75	3·30	0·60	0·34
Os Ir	0·11	2·65	tr.	1·50	2·80	2·51	3·77	14·62	4·95	—	0·95	8·86
Chromite	—	—		—	--	—	1·27	1·95	—	—	—	—
Ru	—	—		—	-	—			—	—	1·40	—
Au	--							-	0·55	—	0·95	3·97

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[1] *Chem. Centralblatt*, 1877, p. 287.

[2] *Loc. cit.*

Besides occurring native, or in alloys, platinum is found in very small quantities in fahl-ores, zinc blendes, lead, silver and uranium ores, and in various rocks. For instance Rössler has found 0·0058 per cent. of platinum in the *Blicksilber* of Commern and Mechernich.

THE EXTRACTION OF PLATINUM

The extraction on the large scale is preceded by a concentration of the ore by washing. If gold is present it is concentrated with the platinum by the same process. Gold is removed from the residue by mercury, which amalgamates with this metal and does not affect platinum. For example, at Nischni-Tagilsk the washed sand is first divided into two portions, one rich, the other poor in gold. Each of these portions is placed in bowls of wood, iron, or porcelain (in quantities of 11 to 30 lbs.), and rubbed up with mercury for half an hour. After this, the amalgam formed is poured out, and this rubbing with mercury repeated until the whole of the gold has been extracted.

Then the further treatment may be conducted either in the dry or the wet way. The dry way does not produce pure platinum, but its alloys with iridium and rhodium. The production of pure platinum requires the use of a wet method. Electrolysis is used to separate metallic platinum from its alloys with gold.

The wet method is principally used.

EXTRACTION OF PLATINUM IN THE DRY WAY

Two methods have been elaborated by Deville and Debray.[1] One consists in melting the ore in a vessel made of lime, and re-melting the button thus obtained: the second method is to melt the ore with galena and litharge in a reverberatory furnace and scorify the lead-platinum alloy obtained in order to remove the lead. Lastly the platinum is fused into an ingot in the lime furnace.

The melting of the ore in this lime vessel, known as the Deville furnace, is achieved with the help of an oxy-coal-gas flame.

The arrangement of this method of melting is shown in Fig. 341.

The vessel consists of two halves formed out of a hollow cylindrical block of calcined lime. In the hollow *b* the ore is placed, through an opening in the upper half, not visible in the figure. This opening is closed by a lime stopper during the melting. A second conical opening *q* serves to admit the current of gas. This latter is led to the opening through a platinum tube which has a perforated tip at its lower end. This tube is attached at its upper end to a copper one *c*. Through the tube *h*, the coal gas, and through the tube *o*, the oxygen are introduced. The products of combustion escape through the opening *d*; the same opening serves for pouring the molten mass. There is a proper arrangement of taps to both gas pipes, so as to make the flame oxidising or reducing.

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[1] Dingler, vol. 153, p. 38; vol. 154, pp. 130, 199, 287, 383; vol. 165, pp. 198, 205.

After a small portion of the ore, previously warmed and mixed with some chalk, has been put in through the opening mentioned, it is melted in an oxidising flame. Metals other than the noble ores are thus oxidised and form, with the chalk and any gangue present, a slag, which is absorbed by the lining of the vessel. Any volatile compounds or powdery substances escape with the products of combustion.

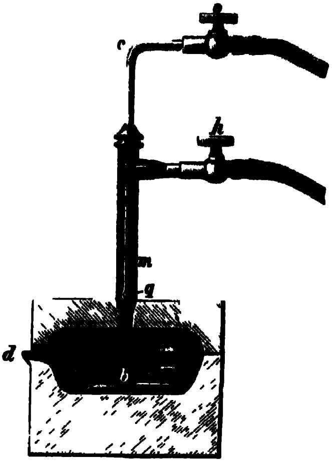

FIG 341

To this molten mass ore is now added in small portions until the lower part of the cavity is filled with molten metal. It is then poured out and remelted in another Deville furnace with an oxidising flame, so that again part of the commoner metals are oxidised and absorbed by the lime. The continual use of a fresh furnace is rendered necessary by the decreasing power of absorption of the lime for the slag. Finally, there is obtained, not pure platinum, but an alloy with iridium and rhodium, from which pure metal can be obtained by a wet method.

The second method by Deville and Debray separates platinum from the ore by the help of lead, which alloys with platinum but not with osmiridium.

For this purpose about 1 cwt. of the crude platinum is melted in a reducing flame, with the same quantity of galena, in a small reverberatory furnace, on a hearth composed of marl or calcium phosphate, about 3 feet 3 inches long, 6 inches medium depth, and 20 inches broad. The galena is decomposed by the iron present in ,the ore, a lead matte is formed and metallic lead set free, which alloys with platinum. To decompose the matte about 2 cwt. of litharge are added, the heat increased and the whole covered with fusible glass. The lead matte is reduced to lead by the litharge, and again forms the platinum alloy, while sulphur dioxide is given off. Osmiridium, which does not alloy with lead, remains at the bottom of the furnace. After the slag containing lead has been skimmed off, the alloy is removed by a cast-iron ladle. The lower part of the bath containing the osmiridium is added in the working of another portion of ore, so as to enrich it. Finally, this lower portion is poured out on to a gently sloping surface, on which the platinum-lead alloy will run down while the osmiridium remains.

The former is removed to a refining furnace provided with a blast. In proportion as the lead is removed the temperature must be further raised. It is not, however, possible to remove the whole of the lead while the material remains liquid, as it solidifies whilst lead is still present.

The residue is melted in the Deville furnace already described; in this the lead and any other volatile elements are volatilised away, and the commoner metals are oxidised and passed into slag. Rhodium and iridium remain with platinum. The platinum is poured into moulds lined with sheets of the metal.

To melt larger quantities of platinum (more than 9 lbs.), the vessel shown in Figs. 342 and 343 is used. It consists of a cylinder of sheet-iron lined with lime, and with the cover shown in Fig. 343. A stream of oxy-coal-gas is led through the hole in this cover. The vessel can be tipped to pour out platinum. In this Deville and Debray melted about 25 lbs. of Russian coins with the use of 4·2 cubic feet of oxygen.

The Siemens[1] electric furnace, which was expected to be of great service in fusing platinum, has not fulfilled expectation, because platinum always absorbs carbon from the carbon electrodes of the furnace, and thus loses most of the properties that are of value in the arts.

Up to the present time the dry method of obtaining platinum has only been used exceptionally.

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[1] *Allgemeine Huttenkunde*, p. 256.

EXTRACTION OF PLATINUM BY WET METHODS

This method of extraction consists essentially in bringing platinum into solution with aqua regia, precipitating from this solution platinum-ammonium chloride by means of ammonium chloride and ammonia, and then decomposing this compound and separating platinum at a red heat.

This process, invented by Wollaston, was formerly carried out with slight variations at the laboratory of the Department of Mines at St. Petersburg. There the ore was treated for 8 or 10 hours in open vessels, on a hot sand-bath, with 10 or 15 times its weight of aqua regia (composed of 3 parts hydrochloric acid at 25° B. and 1 part nitric acid 40° B.). By this means platinum, a portion of its kindred metals, and baser metals were brought into solution, while osmiridium chiefly, with rhodium and ruthenium, and small quantities of iridium and palladium, remained behind with the sandy residue.

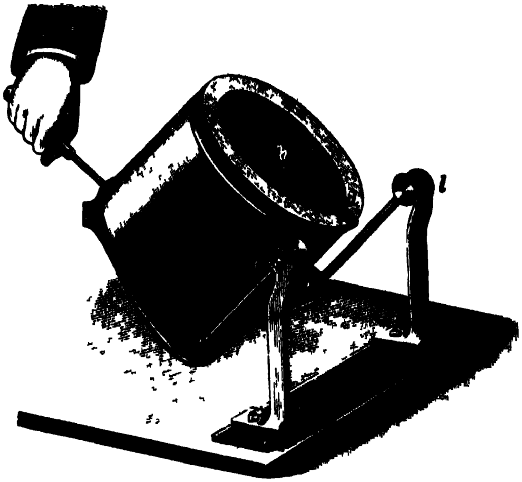

Fig. 842

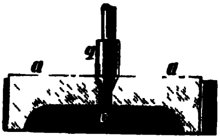

Fig. 843

The solution which contained besides platinum, iridium, rhodium, palladium, copper, iron, and small quantities of osmium and ruthenium was treated with solution of sal-ammoniac in glass vessels to precipitate the platinum as double chloride. In this process it was necessary for the solution to contain excess of acid to prevent a precipitate of iridium from coming down.

The precipitate of double chloride was washed and dried and strongly heated in platinum vessels, whereby it is converted into platinum sponge. This sponge is triturated, sieved, pressed together in a screw press with steel dies, and then strongly heated for 1½ days in a porcelain furnace. This red-hot platinum was hammered into bars or rolled into sheets.

The first part of the wash-water obtained in washing the platinum-ammonium chloride precipitate was evaporated down to one-twelfth its original volume, when a similar iridium salt containing platinum crystallised out, and, on heating, yielded a platinum-iridium alloy. The second part of the wash-water was evaporated completely to dryness, heated to redness, and added to a fresh portion of ore when the latter was treated with aqua regia.

Since the platinum obtained in this process was not free from iridium, Döbereiner's[1] method to obtain platinum without iridium was used. The platinoid-metals, but not platinum itself, are precipitated by treating the aqua regia solution diluted to 35° B., with lime water until the reaction is only feebly acid. But this process gave neither a precipitate of the platinoid metals free from platinum, nor platinum free from them.

Schneider,[2] in order to avoid the precipitation of iridium with platinum, treats the ore with aqua regia and excess of hydrochloric acid, and evaporates the solution obtained nearly to dryness. The liquid is then diluted with water, treated with soda until it is fairly alkaline, and boiled with alcohol. The precipitate obtained is dissolved in hydrochloric acid. From this solution platinum can be precipitated by ammonium chloride as the pure double chloride. By this method iridium and rhodium are converted into sesqui-chlorides, which are not precipitated by sal-ammoniac. It is not known yet how far this process has come into use.

Heræus in Hanau,[3] in order to make the ore dissolve more quickly, places it in glass retorts with a mixture of 1 part aqua regia with 2 parts water, under a pressure of 12 inches of water, evaporates the solution, and heats the residue obtained to 125°, so that the sesqui-chlorides of iridium and palladium are formed. Then this residue is dissolved in hydrochloric acid. Next the pure double chloride is precipitated from the solution. This is converted into platinum sponge by ignition, and the sponge melted in a lime crucible. The liquid filtered from the platinum double chloride precipitate is evaporated to a certain density, when the iridium salt comes down. The remaining metals are precipitated from this solution by iron turnings. The excess of iron is removed from the precipitate by hydrochloric acid, and the latter is then treated with aqua regia in order to obtain more of the platinum and iridium precipitates.

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[1] Liebig's *Annalen*, vol. 14, 10, 251.

[2] Dingl. 190, 118.

[3] *Amtl. Bericht über die Wiener Weltausst. i. J.*, 1873, vol. iii. 999. Dingl. vol. 220, p. 95.

Palladium, rhodium, ruthenium, osmium and iridium may be obtained from the residues after the ore is dissolved, and from the mother liquors after precipitation.

G. Matthey[1] produces pure platinum from the commercial crude metal by melting it with six times its amount of lead, granulating this alloy, and treating it with dilute hydrochloric acid, which dissolves iron, lead, palladium and rhodium, while platinum remains behind with iridium, and small quantities of lead, rhodium and other platinoid metals. This residue is boiled with aqua regia, when platinum and lead dissolve and iridium remains behind. The lead is precipitated by sulphuric acid. The liquid is filtered from lead sulphate, and treated with excess of ammonium chloride and common salt to precipitate platinum in the usual way. If rhodium is present in the solution, the precipitate is rose-colour instead of pure yellow. It is ignited with bisulphate of potash, which forms rhodium-potassium sulphate, while the platinum separates as metal. The double salt is dissolved by boiling the whole with water.

To hasten the separation of platinum and minimise the quantity of aqua regia, it has been proposed by Hess,[2] and by Dullo,[3] to melt crude platinum with four or five times its weight of zinc, and treat the alloy with sulphuric acid first.

Wyott[4] has brought forward a process for extracting the platinoid metals from residues and mother-liquors. Platinum, palladium and rhodium are dissolved out of the ores by aqua regia. The first is precipitated by ammonium chloride. The liquid is filtered off neutralised by soda, and palladium cyanide ($PdCy_2$) precipitated from it by mercuric cyanide. Rhodium remains in the solution. The residue after treatment with aqua regia is to be heated in a stream of air, whereby osmium is converted into tetroxide, which volatilises, and rhodium oxide is deposited in the hotter parts of the exit tube. The residue, after this heating, is mixed with salt and heated in a stream of chlorine. Sodium-iridium chloride is formed, which is dissolved by boiling water.

When gold is precipitated from an aqua regia solution by iron chloride (described under Gold[5]), the solution which remains consists of iron chloride, which, together with finely divided gold, in many cases contains also platinum, palladium and chloride of silver finely divided, while iridium, ruthenium, rhodium, selenium and various base metals are in the solution. From these materials platinum and the platinoid metals are extracted at the gold and silver works at Frankfort-on-Main by the following process.[1]

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[1] *Chem. News*, 1879, xxxix. No. 1,013, p. 175. *B. u. H. Ztg.*, 1880, p. 28.

[2] *Erdm. Journ.*, vol. 40, p. 498.

[3] *Erdm. Journ.*, vol. 78, p. 369.

[4] *Engin. and Min. Journ.*, 44, p. 273.

[5] *See* vol. i., pp. 862, 863.

Sheet-iron cuttings are first placed in the solution in order to reduce ferric to ferrous chloride, which can be used again to precipitate gold. The iron throws down selenium and the metals mentioned, in the form of a black mud, which is removed from time to time from the vessels (large stoneware pots). After the larger pieces of iron have been sieved out of the mud, it is digested with iron chloride to remove iron and copper, and then repeatedly washed with dilute hydrochloric acid. It is next dried and smelted with soda and coal. A button of metal is obtained, and a slag containing selenium, which is collected and worked up for that element. The metallic button is re-melted and granulated, then digested in glass retorts with aqua regia containing excess of hydrochloric acid, by which means the greater part of any copper present is removed. It is necessary for this purpose to use a limited quantity of the acid mixture, as otherwise copper and all the noble metals will be dissolved, and the presence of copper will make the precipitation of platinum and palladium difficult. The noble metals that pass into solution are separated again by the metallic copper present in the granules or by copper wire put in for the purpose. Finally, the solution contains principally cuprous chloride, kept dissolved by the excess of hydrochloric acid, and also some cupric chloride. After the metallic mud has been nearly freed from copper by this operation, repeated if necessary, it is boiled with aqua regia, and all the metals brought into solution. When this is diluted with water, antimony is thrown down as oxychloride. The diluted solution is afterwards brought back to its former concentration by evaporation, and the gold is thrown down by an electric current. (Gold must not be thrown down by ferrous chloride, which would bring back iron into the solution.) Next, platinum is precipitated by sal-ammoniac, and the precipitate, after ignition, gives the metal with only 0·005 per cent. impurity. The filtrate from this last precipitate still contains sal-ammoniac, and is used to precipitate platinum from another solution, whereby the quantity of iridium and palladium dissolved in it is increased. Afterwards, this enriched solution is evaporated until the iridium-ammonium chloride separates out, and, lastly, from this mother liquor the similar palladium double salt is crystallised out by adding ammonia and hydrochloric acid.

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[1] *Dingl. Journ.* 224, p. 414.

The usual composition of platinum metal is given by the following analyses[1]:—

	I.	II	III.
Pt	99·20	99·9	99·9
Ir	0·32	-	-
Rd	0·13	0·01	
Pd			—
Ru	0·04		-
Fe	0·06		0·0001
Cu	0·07		—
As	-	0·01	

The origin of the first sample is unknown, the second is from Johnson, Matthey and Co.'s works in London, and the third from the works of Heræus in Hanau.

EXTRACTION OF PLATINUM BY AN ELECTRO-METALLURGICAL METHOD

By this method platinum and its allied metals are removed from their alloys with gold. Further, platinum can be separated from iridium and rhodium by a weak current acting on an acid solution of platinum chloride as the electrolyte. As, however, platinum separates easily from most of its compounds by simple heating, the electrolytic method seems unnecessary in this case The separation of gold and the platinum metals is carried out on a large scale at the North German Refinery at Hamburg. The complete process is a secret. The alloys concerned are used as anodes in the form of sheets. Gold leaf forms the cathodes, and a neutral solution of gold chloride the electrolyte. Chemically pure gold is deposited on the cathode, while, as the anode dissolves, the platinoid metals are unacted on, and fall as a black mud to the bottom of the cell. Nothing is known of the exact composition of the alloy, the strength of the current, or the electric potential.

In the electrical refining of copper from the Sudbury ores (containing sperrylit), the anode mud produced contains platinum. nothing has been made known as to the further treatment of this mud.

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[1] *Mineral Industry*, 1892, p. 384.

ALUMINIUM

Physical Properties

Aluminium has a tin-white colour and high lustre. If a minute quantity of silicon has been allowed to remain in it, the colour has a bluish tinge, a larger quantity makes it gray. Mechanical treatment also produces a bluish tinge.

The fracture of cast aluminium shows a coarse fibre and irregular grain, while it is sinewy or fine-grained, and shows a high silky lustre after being hammered and rolled.

According to Deville, aluminium crystallises in regular octahedra if slowly cooled. According to Rose the crystals do not belong to the regular system.

The specific gravity of aluminium is considerably less than that of all other metals used generally in commerce. At 22° C. it is 2·64 for cast metal, 2·7 for drawn metal.

It has the softness of silver, but clogs like lead or tin when filed, turned or planed. It is also tenacious enough to be beaten into the thinnest sheets and wire like silver.

It is malleable both when cold and hot. It is possible to hammer out in the cold a stick of aluminium of 80 units section into one of single unit section, without any tearing on the edge; but hammering and extending in the cold diminish the malleability of the metal and increase its hardness. To keep its malleability unaltered it must be worked when hot. It is subjected to cold hammering and rolling when its strength and hardness are to be increased.

Aluminium has considerable tensile strength, which is greatly diminished by heating. In cast aluminium it comes near to that of ordinary iron (6 to 7½ tons to the square inch, with 3 per cent. extension). Cold rolled, or hammered metal has a tensile strength equal to that of cast gunmetal, and greater than that of hot rolled copper. Bauschinger in Munich has given the strength of cold pressed and hammered aluminium as 17 tons per square inch, with a diminution of section from 12·9 to 1.

The diminution of the tenacity of the metal with increasing temperature has been tabulated by André le Chatolier[1] ;—

Temperature	15°	100°	200	300°	400°	460°
Tenacity in lbs. per sq. in	25,770	20,946	13,890	7,937	3,307	2,205

Aluminium is distinguished by a clear ringing sound. Its electric conductivity is given as 59 when pure copper is 100 Its specific heat is 0 202.

It melts at a red heat between 600° and 700°. At a higher temperature it volatilises, but the exact boiling point has not yet been accurately determined As its specific heat is high it needs much heat and some time to fuse, and as its latent heat is also great it takes a long time to cool and solidify According to Deville, when it is cast into small bars, it is several hours before these can be held in the hand. There is a diminution of volume during solidifying, the shrinkage being 1·8 per cent of the original volume.

Aluminium may be readily plated with gold and silver. There are great difficulties in the way of plating with iron, copper or brass.

With regard to the influence of other elements in small quantity on the properties of aluminium, it is well known that 1 to 2 per cent. of silicon does not render the metal noticeably less soft and tenacious in the cold, but decreases its malleability when hot. More than 2 per cent. of silicon makes the metal brittle and short.

Quite small quantities of carbon seem to deteriorate the valuable qualities of the metal altogether.[2]

Large quantities of iron make it hard and brittle. Aluminium with 10 per cent. of iron is as brittle as native sulphide of antimony.

Nickel in quantity has the same effect; with 3 per cent. aluminium is still workable, but harder and more elastic than when pure.

Zinc in quantities above 3 per cent. renders it hard and brittle, with less than 3 per cent. of zinc the metal is harder than when pure, but still very workable.

Bismuth also produces brittleness. With only $\frac{1}{10}$ per cent. aluminium shows clefts under the hammer even when repeatedly annealed.

Copper in quantity has the same effect, but up to 5 per cent. leaves aluminium still workable. With 10 per cent. it is as brittle as glass. Copper containing aluminium is hard, elastic, and easily rolled both cold and warm.

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[1] Dammer, *Chem. Technology*, vol. 2, p. 204.

[2] Borchers, *Elektrometallurgie*, p. 98.

CHEMICAL PROPERTIES OF ALUMINIUM AND OF ITS COMPOUNDS WHICH ARE IMPORTANT IN ITS EXTRACTION

Compact aluminium does not oxidise in either wet or dry air at the ordinary temperature. When melted it oxidises very slightly and becomes covered with a thin deposit of the sesquioxide, which prevents further action. It is, however, easily oxidisable when in fine division or in thin leaves; it then burns, if heated in a gas-flame, with a dazzling light, and forms the sesquioxide. If it is fused with saltpetre, it is not oxidised at a dull red heat, but forms potassium aluminate when further heated. At a strong white heat it burns superficially to form the sesquioxide, but here again a thick layer of this oxide stops further action.

When melted it reduces many oxides, for example, those of iron, lead, copper, carbon, silicon and boron, forming alumina. Any aluminium remaining combines with the element thus separated. Alumina, the sesquioxide, is not soluble in metals, and does not deteriorate them when present; therefore aluminium forms a good agent for purifying metals containing their oxides, and superior to other elements similarly used for refining (such as silicon, phosphorus, manganese, magnesium and sodium).

Aluminium is not attacked by water, either when boiling or at the ordinary temperature. At a red heat steam hardly attacks it; at a white heat only superficially and slightly.

Aluminium leaf boiled for many hours with pure water is entirely converted into alumina, hydrogen being set free.

Mylius and Rose[1] find that water containing air acts upon aluminium so that small quantities of hydrogen dioxide are formed which disappear during the oxidation of the metal.

At a high temperature sulphur combines directly with the metal to form the sulphide (Al_2S_3), while sulphuretted hydrogen has no action on it. In this respect aluminium has an advantage over silver, which is blackened by sulphuretted hydrogen, the sulphide being formed.

Chlorine, bromine, iodine, boron and silicon combine easily with aluminium.

It is hardly attacked by dilute sulphuric acid, but dissolves in the hot concentrated acid.

Nitric acid, whether dilute or concentrated, does not act on it in the cold. It is slowly dissolved by the boiling concentrated acid. Hydrochloric acid dissolves the metal, more easily in proportion as more concentrated; it therefore forms the best solvent. Potash and soda lye dissolve the metal energetically; hydrogen is given off and potassium or sodium aluminate formed. Fused alkalies, with not more than one equivalent of water, do not attack aluminium.

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[1] *Zeitschr. f. Instrum.*, 1893, p. 77.

Aqueous ammonia attacks it only slightly, gaseous ammonia not at all. Lime water acts like potash and soda lye. Organic acids have no action in the cold, and only a very feeble one when warmed.

Finely divided aluminium will burn with flame in a stream of chlorine, forming the chloride.

The metal is attacked by aqueous solutions of the carbonates, phosphates, silicates, borates and sulphides of the alkalies.

A solution of aluminium chloride acts energetically on the metal, forming a basic chloride. A solution of alum mixed with common salt dissolves aluminium, giving off hydrogen, and forming a basic chloride.

Aluminium does not throw down any electro-negative metal from its solution as sulphate; it does slowly, and with difficulty, deposit them from their nitrates, but quickly and readily from their chlorides (for instance, silver, copper, mercury, lead, thallium).

It precipitates silver, lead and zinc from their alkaline solutions.

Amongst the materials used as fluxes, carbonates and sulphates of alkalies, also silicates and borates, are found to have a specially injurious effect on aluminium. Silicon and boron will be set free from the two last; and silicon combines in all proportions with aluminium, and is always taken up, if excess be present. Silicates and borates should, therefore, not be present during the production of the metal. Haloid compounds of aluminium attack the metal. The least injurious fluxes are common salt and calcium fluoride.

It is best to fuse aluminium without any flux.

ALUMINIUM OXIDE: ALUMINA (Al_2O_3)

is found naturally as corundum, sapphire and emery. It is obtained artificially, by igniting the hydrate, in the form of an amorphous white powder, which is insoluble in water, and difficultly soluble in acids. It may also be obtained in the same form by igniting aluminium sulphate, and ammonia-alum. It melts at a very high temperature to a clear, colourless liquid. It is split up by an electric current into aluminium and oxygen. It is reduced to metal by carbon at the high temperature of the electric current. It acts as acid radicle to many bases (alkalies and alkaline earths), and forms aluminates. The best known is sodium aluminate, $Al_2(NaO)_6$.

Alumina forms several hydrates with water, from $Al_2O_2(OH)_2$ to $Al_2(OH)_6$.

These hydrates occur naturally as diaspore, bauxite and hydrargillite. Artificially, a hydrate is obtained by precipitation from an alkaline aluminate with carbon dioxide. Thus with sodium aluminate:

$$Al_2(ONa)_6 + 3H_2O + 3CO_2 = Al_2(OH)_6 + 3Na_2CO_3.$$

This gives a loose white powder soluble in acids. It acts as an acid with oxides of the alkalies and alkaline earths.

ALUMINIUM CHLORIDE (Al_2Cl_6)

is obtained by burning the metal in chlorine. In Oerstedt's method it is obtained by igniting an intimate mixture of alumina and charcoal in a stream of chlorine:

$$Al_2O_3 + 3C + 3Cl_2 = Al_2Cl_6 + 3CO.$$

If the hydrate is dissolved in hydrochloric acid and the solution evaporated, the anhydrous chloride cannot be obtained, as the solution splits up into alumina and hydrochloric acid. Aluminium chloride is colourless, gives off vapours in the air, and absorbs moisture from it. At high temperatures (below its melting point), it volatilises easily. If these vapours act upon aluminium at a red heat in an atmosphere of oxygen, the oxychloride is formed. If aluminium is heated to 1,300° in a tube containing vapours of the chloride in the absence of air, small drops of the fused metal are deposited in the cool parts of the tube (Troost and Hautefeuille). The explanation seems to be that a gaseous lower chloride is formed, and then decomposed.

Aluminium is not successfully separated from the chloride by an electric current, because this compound volatilises before it fuses. The decomposition goes on properly, however, if the easily fusible double chloride with sodium is used. This double salt was formerly used to obtain the metal. Aluminium fluoride can be obtained according to Grabau, by decomposing cryolite ($Al_2F_6 6NaF$) with aluminium sulphate, sodium sulphate being formed at the same time. The substance obtained is a white powder, insoluble in water. It is decomposed by sodium at a red heat, aluminium in the metallic form being deposited while an artificial cryolite (aluminium and sodium fluoride) is formed. Grabau bases his method for extracting aluminium upon this reaction.

ALUMINIUM CARBIDE

It was formerly thought that aluminium did not combine with carbon. Moissan[1] has very recently succeeded in making a compound of the formula C_3Al_4, by heating them in an electric furnace in an atmosphere of hydrogen. The substance forms yellow transparent crystals.

According to Borchers,[1] when alumina and coal are heated in an electric furnace, a gray sintered mass is obtained, which, when cold, is brittle and crumbling, and consists of aluminium, aluminium carbide, carbon, and various impurities originating in the coal.

He states also that quite small quantities of carbon will render aluminium unfit for commercial use.

Salts in which aluminium acts as a base are derived from the oxide Al_2O_3. The metal is not precipitated by other metals from the aqueous solutions of these salts. It has not so far been separated by an electric current. The hydrate, and not the metal, is thrown down when the solutions are electrolysed.

SILICON-ALUMINIUM

is obtained when aluminium is melted with silicates. In this way a compound containing 70 per cent. silicon can be obtained. A portion is dissolved in the aluminium, and another part seems to be mechanically mixed like graphite in pig-iron. When silicon-aluminium is treated with hydrochloric acid, part of the silicon escapes as siliciuretted hydrogen, another passes into solution as silica, and a third part remains behind as a black powder.

ALLOYS OF ALUMINIUM

Aluminium alloys with most metals. It combines easily with potassium and sodium. An alloy containing only 2 per cent. sodium decomposes water.

It also alloys with calcium and magnesium.

It combines with iron in all proportions, and separates carbon from it very much as silicon does. The alloy is very hard and brittle. Aluminium present in iron in small quantities lowers its melting point, and increases its strength, hardness and ductility.

It behaves in the same way with nickel and cobalt, the alloys being brittle. But an alloy containing up to 3 per cent. nickel can be worked, and is harder and more elastic than pure aluminium.

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[1] *Zeitschr. für Elektrotechnik und Elektrochemie*, 1894, vol. vi.; *Comptes Rendus*, vol. cxix., 1894, part i., p. 16.

[2] *Elektrometallurgie*, p. 98.

It easily unites with zinc, of which more than 3 per cent. produces brittleness. Alloys of zinc, copper and aluminium are used to solder aluminium.

Alloys with tin are also easily formed; and are used to solder aluminium. Lead and antimony combine very imperfectly with aluminium.

Bismuth easily unites with it, forming brittle substances, very quickly oxidised at the ordinary temperature.

Copper and aluminium form alloys in all proportions. Whilst a little copper deteriorates aluminium, and 10 per cent. makes it as brittle as glass, on the other hand a small proportion of aluminium improves copper. Copper containing up to 10 per cent. aluminium is distinguished by great hardness, strength and tenacity, and, under the name of aluminium bronze, has found manifold technical uses where these qualities are essential. The bronze comes into competition with tombac, phosphor-bronze, manganese-bronze, delta metal and steel.

If the copper contains more than 10 per cent. of aluminium, the alloy will be brittle. Below 10 per cent. the tenacity increases rapidly. Cast aluminium bronze, containing 5 per cent. aluminium, breaks at a strain of 25 tons per square inch with an extension of 64 per cent. on a 4 inch specimen. An addition of silicon increases the former to 50 tons per square inch, and decreases the latter to 1 per cent.

The colour of the bronze is bluish-white if there is more than 20 per cent. of aluminium; with between 20 and 15 per cent. of this metal it is pure white; with less proportion of aluminium it gradually becomes yellow; 5 per cent. gives a gold yellow; 3 per cent., a red gold colour.

The melting point of bronze with 10 per cent. of aluminium is about 950°; it makes good castings.

A small quantity of aluminium (1 to 2 per cent.) has a good effect on brass; it makes it more limpid when molten, and increases its strength and tenacity.

Aluminium does not unite directly with mercury, apparently because the first attack of the mercury is prevented by the slight film of oxide on the surface of the metal. An amalgam is formed when aluminium forms the cathode in the electrolysis of a mercury salt, or if the metal is moistened with caustic alkali, or if its surface is scraped under mercury. It loses its lustre in the amalgamated state, and in the air forms the oxide with evolution of heat.

An alloy of equal quantities of aluminium and silver is as hard as bronze.

Gold containing 1 per cent. of aluminium has a green colour, with 10 per cent. it is white and brittle; with 22 per cent. deep purple, and possesses a melting point about 20° C higher than that of pure gold.[1]

MATERIAL FOR THE EXTRACTION OF ALUMINIUM

Aluminium, after oxygen and silicon, is the most abundant element on the globe, yet there are very few minerals which lend themselves to its extraction

The most common, clay, felspar, mica and kaolin, and the rocks of which these minerals form the constituents, have not yet been utilised at all to produce aluminium

Bauxite, cryolite, and minerals containing aluminium sulphate, are the only proper aluminium ores Corundum has been used so far only in making alloys.

Bauxite is a mixture of aluminium and ferric hydrates, and was first found in the district Baux, near Arles, in Provence. It was discovered later on in other parts of the South of France It also occurs in the Departments Var and Bouches du Rhône over a length of 95 miles in beds of a thickness amounting in places to between 65 feet and 95 feet.[1] Beds have also been found in Carniola, Nassau-Hesse, Ireland, Calabria, Senegal, Georgia and Alabama.

The composition of various kinds of French bauxite may be seen in the following analyses:[2] No. I is from Villeveyrac (Hérault), II from Nas de Gilles at Baux, III. from Paradon at Baux, IV. is a silicated bauxite at Villeveyrac, V a silicated bauxite from Baux

	I	II	III.	IV	V
Alumina	78·10	57·6	—	43·20	58·1
Alumina with titanic acid	—	—	18	—	—
Ferric oxide	1·02	25·3	60	7·25	3·8
Silica	5·78	5·9	4	34·40	24·9
Water	15·10	—	--	15·15	14·2
Water and calcium carbonate	-	11·2	18	—	

The following is the composition of a German bauxite from Muhlbach, near Hadamar, in Nassau-Hesse —

Alumina	55·610
Ferric oxide	7·170
Silica	4·417
Chalk	0·386
Magnesia	trace
Water and loss by heat	32·330

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[1] W. C. Roberts-Austen, *Proc. Roy. Soc*, 1892, p 367

[2] *Revue Univ. des Mines*, 1863, xiv, 387.

[3] Knab, *Métallurgie*, p. 581.

The following are three specimens of a variety called wochenite from Feistritz, in Carniola, analysed by G. Schnitzer.

	Brown Wochenite.	Yellow Wochenite.	White Wochenit
Alumina	44·4	54·1	64·6
Ferric oxide	30·3	10·4	2·0
Silica .	25·0	12·0	7·5
Water and loss by heat	9·7	21·9	24·7

Bauxite is first converted into alumina, which is the proper material from which to extract the metal.

Cryolite, a double fluoride of sodium and aluminium of the formula Al_2F_6+6NaF, occurs at Ivitut in the Bay of Arsuk in South Greenland, where it forms an extensive deposit. At the surface it is white, at 10 feet deep it is blue-green, at 15 feet it is black, and transparent at the edges. The darker kinds become white when ignited.

The composition of pure cryolite is as follows:—

Aluminium	13·07	per cent.
Sodium	33·35	„
Fluorine	53·58	„

Cryolite can be worked up directly into the metal, or first converted into the oxide.

Alum can be obtained from certain rocks and minerals containing aluminium sulphate; it is used as a source of alumina, and from the latter the metal is obtained. Such minerals are *alum-earth*, *alum-shale*, *alum-stone* or *alunite*, *hair-salt* or *alunogen*, *aluminite*. *Corundum*, which forms rubies and sapphires when in its purest forms, is used as an ore for aluminium in its impure form, in which it is known as emery. This is found at Naxos in Greece, and at Chester in Massachusetts, and has recently been discovered in large quantities in the States of North Carolina and Georgia.

THE EXTRACTION OF ALUMINIUM

Aluminium can be obtained in the dry way and by electro-metallurgy. Its extraction in the wet way, as a deposit from aqueous solution, has hitherto been found impossible, as no metal has been found to precipitate it; neither has its deposition from such solution by an electric current been found possible.

The extraction by a dry method is confined to the decomposition of certain fused halogen compounds of the metal by sodium, or magnesium. Aluminium is then separated as metal, while the sodium or magnesium combines with the halogen. Such compounds are the double chloride of aluminium and sodium, cryolite ($Al_2F_6 6NaF$), and aluminium fluoride (Al_2F_6), which are chiefly used in the production of the metal.

The process in which the double chloride of aluminium and sodium is used is the oldest. It was used for a long time, but it is costly, and has been supplanted by an electro-metallurgical method.

The process of separation from cryolite by sodium was used only a short time; the cost was too great, and the yield of metal from cryolite, which contains only 13 per cent., is too small.

The production of aluminium from the fluoride (Grabau's process) has hardly yet come into definite use.

Apart from these processes (of which the two first have been carried out with most varied practical modifications), there has been no lack of proposals for the extraction Some of these have never been tried at all, and others have not been able to survive trial. these may therefore be passed over.

Electro-metallurgical methods have been confined up till now to fusible compounds of the metal, in contradistinction to aqueous solutions. Such compounds are first fused and then decomposed by an electric current. The sources employed are alumina, the haloid compounds, and the sulphide. A separation of the metal from its silicates has not been achieved so far. The fact that the current may be used first to fuse the halogen compounds causes a considerable economy in the process, so that the other methods, in which such compounds have to be fused and then reduced by sodium, cannot compete with this one, and are falling into disuse.

The production of pure aluminium on a large scale by an electric current has only quite recently been achieved. The difficulties arose from the aluminium taking up carbon from the carbon cathode, or from the carbon used to reduce the alumina; from the volatilisation of part of the metal; from difficulty in collecting the metal into a solid mass; and from the aluminium vapour being caused to ignite by carbon monoxide.

The precursors of the method for making pure aluminium were those for producing aluminium alloys by the electric current, particularly Héroult's process. This consists in fusing alumina by the current, and electrolysing it between sticks of carbon as anodes and fused metals as cathodes. Aluminium is deposited at the cathodes and combines with the fused metal there to form an alloy. The oxygen set free at the anode burns with the carbon there to carbon monoxide.

Previous to this process for making alloys, a similar one, invented by Cowles Brothers, was carried on to a large extent in the United States. In this, however, opinions differ as to the action of the current. A mixture of alumina, wood charcoal, and the metal (or the oxide of the metal), with which the aluminium was to be alloyed, was subjected to the action of a current between two carbon poles. Aluminium was separated, and combined with the metal, which was usually copper, to produce aluminium bronze.

Authorities are not agreed as to the exact action of the current in this case, whether it is solely electrothermic or partly electrolytic also. In the first case the alumina is reduced by carbon, in the second it is split up by the current into aluminium and oxygen Hampe[1] has concluded, as the result of his own experiments, that the action is at first electrothermic, but afterwards essentially electrolytic. Borchers[2] takes the view that the alumina is reduced to metal by the electrically heated carbon. He bases his decision on a simple experiment, which is described below

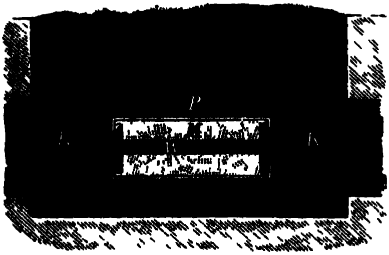

FIG 344

A thin carbon pencil *W* (Fig. 344) of about one-eighth of an inch in diameter and two inches long, is made fast between two strong sticks of carbon *K* one inch or one and a quarter inch in diameter. This pencil passes lengthwise through a small cylindrical paper shell *P*, filled with an intimate mixture *M* of alumina and charcoal (obtained by repeated mixing and igniting aluminium hydrate and tar). Two small cork discs close the ends of the cartridge. After the latter is well covered by coarsely-powdered wood charcoal, the whole arrangement is put into a circuit in which a current of 35 to 40 amperes is passing, and remains there two or three minutes. The cartridge thus heated is sufficiently cooled, and when the charcoal powder has been removed the central pencil is found to be covered with a sintered mass, which consists of aluminium strongly impregnated with carbon. The absolute impossibility that a spark should be produced in this experiment will be quite obvious, and there can be no sign of an electrolytic decomposition as long as there is no break in the current within the mixture. It need hardly be mentioned that if copper or copper oxide be added to the mixture aluminium bronze will be produced. With this simple arrangement it is an easy matter to show by experiment that every metallic oxide is reduced by carbon at a sufficiently high temperature.[1]

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[1] *Chemiker Zeitung*, 1888, p. 391

[2] *Elektrometallurgie*, p. 97

It thus appears that in the Cowles process alumina is reduced by carbon, and that the current simply supplies the necessary heat. This and the Héroult process are described at greater length later on.

Aluminium is principally extracted at the present time by the agency of electricity.

We must classify methods into -

1. Extraction in the dry way.
2. Extraction by the agency of an electric current
3. Extraction of aluminium in the form of alloys.

As it is not possible to refine the metal it must be produced in the pure state. This consideration renders the process one of the most difficult.

1. EXTRACTION OF ALUMINIUM IN THE DRY WAY

Since this method is no longer practised, it will only be necessary to pass the various processes in short review, although they are very important in the metallurgical history of aluminium, and formed for a long time the chief branch of the industry. They are all based on the decomposition of fused halides of the metal by sodium or magnesium, as already mentioned. The oldest process in which aluminium and sodium chloride was used, was invented by Deville and improved by Castner.

In certain works cryolite is used instead of this double chloride, as in Netto's process, and finally Grabau suggested aluminium fluoride.

A. *Deville's Process*

This was based on the experiments of Wöhler, who had obtained aluminium in 1827 by decomposing its chloride by potassium. In 1854 Deville substituted the much more suitable double chloride, replaced potassium by less costly sodium, and so made the production of the metal possible on a large scale.

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[1] *Elektrometallurgie*, p. 104.

The process consisted in heating the double chloride, mixed with cryolite as a flux, with sodium in a reverberatory furnace at a gradually increasing temperature, when aluminium and sodium chloride were formed.

At the Salindres Aluminium Works (Gard), the largest in France, bauxite was the source of the double chloride of aluminium and sodium. It had to be first converted into aluminium hydrate, which was heated alone to 150°, and then converted into the double chloride by ignition with salt and coal in a stream of chlorine gas.

The production of the pure hydrate from bauxite was effected by fusing it with soda to form sodium aluminate, lixiviating this compound with water, and treating the solution with carbon dioxide, which threw down aluminium hydrate. For this purpose bauxite was powdered and intimately mixed with soda, and the mixture fused in a reverberatory furnace of the Leblanc-soda pattern. (A charge consisted of 9½ cwt. of bauxite and 6 cwt. of soda, and was heated five or six hours.) Thus the alumina became converted into sodium aluminate, while the iron oxide was unattacked.

The aluminate was washed out by water in cylindrical vessels of iron plate, with double bottoms and linen filters. The liquid was transferred to special vessels, each holding 264 gallons, and there treated with carbon dioxide obtained from chalk and hydrochloric acid. Sodium carbonate was formed and remained in solution, while hydrate of alumina was precipitated. The vessels were provided with agitators, and had double bottoms, through which steam was led during the precipitation for five or six hours: the temperature was kept up to 70° C.

The precipitate and the solution were brought into a special vessel, in which the former subsided and the liquid was poured off. The hydrate was ready to be converted into chloride after repeated washings. It then contained 47·5 per cent. of alumina, 50 per cent. of water, and 2·5 per cent. of sodium carbonate.

The solution of sodium carbonate separated from the precipitate was evaporated down and used again to convert bauxite into sodium aluminate.

The hydrate of aluminium was next mixed with sodium chloride and finely-powdered wood charcoal, and the mixture made into balls the size of the fist, with a little water, and dried at 150° C. The dried balls were placed in an upright retort of fireproof clay, and heated to a white heat in a current of chlorine. The volatile double chloride of sodium and aluminium was thus produced, and was collected in condensing chambers attached to the retort, while the carbon monoxide formed, and the excess of chlorine, passed off through a chimney.

The arrangement of the apparatus can be seen in Fig. 345. *R* is the retort, *F* the grate, *P* the fire-bridge; *n*, *n*, are the flues, *O* is the opening to admit chlorine, which enters the retort by a porcelain tube; *L* is the condensing chamber for the double chloride, furnished with a movable cover *M*. Sometimes large earthen pots were used instead of this chamber, with covers well luted down. The incondensible vapours were led through a tube in the cover into the throat of the chimney. The balls were placed in the retort through the opening *Z*, closed by a cover. The residue after firing was removed by an opening *V* in the bottom of the retort, closed by a brick slab, forced upwards by means of a screw.

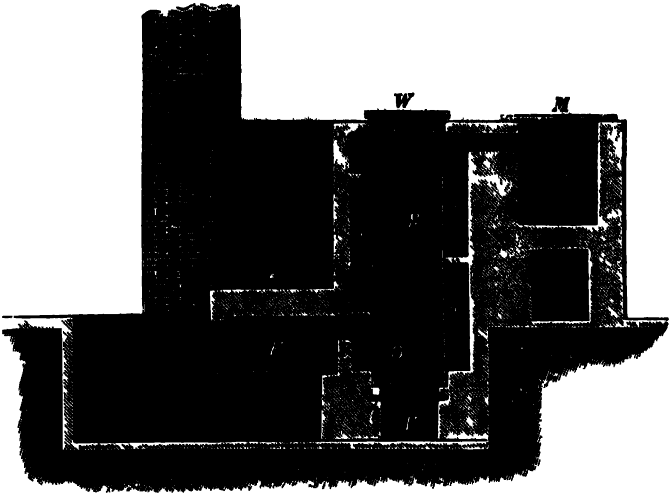

Fig. 345.

After the balls had been put into the retort, heat was applied to remove water from the aluminium hydrate; after it had passed off chlorine was led through and the temperature raised gradually to a white heat. Chlorine was absorbed during the whole operation, and the double chloride appeared in the condensing chamber as a crystalline mass with a yellow colour (due to ferric and ferrous chloride). The reaction is shown in the following equation—

$$Al_2O_3 + 2NaCl + 3C + 3Cl_2 = 3CO + Al_2Cl_62NaCl.$$

One distillation lasted 12 hours. Towards the close the absorption of chlorine became irregular.

The separation of aluminium from the double chloride took place with the assistance of cryolite as a flux. This was necessary to aid the small portions of metal separated to run together. The mixture consisted of 220 lb. of the chloride, 100 lb. of cryolite, 77 lb. sodium. The first two were in the form of powder, the sodium in pieces about $\frac{1}{16}$ to $\frac{1}{8}$ of a cubic inch. The mass, divided into four portions, was charged into a reverberatory furnace with a well and sloping bed at a low red heat. The heat was regularly increased for three hours, after which the separation was complete, and the tapping was proceeded with. First, the slag was run into iron waggons, then the aluminium into heated cast-iron ladles, and, lastly, a mixture of sodium chloride and cryolite containing small portions of aluminium was tapped into another cast-iron ladle. To cast it into bars the aluminium was poured into small cast-iron moulds; the grains of aluminium separated out from the mixture tapped last.

The sodium was produced by heating a mixture of sodium carbonate, coal and calcium carbonate in iron tubes.

In 1882 the cost of production of aluminium by this process was about thirty shillings a pound (80 fr. per kg.).[1] The market price in Berlin in 1885 was about £2 18*s.* per pound (130 m. per kg.). At present it is made by the electric process at less than two shillings a pound (4 m. per kg.).

B. *The Process of Deville and J. Castner*

This is the Deville process improved by Castner. The improvements consist in a cheaper production of alumina and of sodium, in making chlorine by the Weldon process, in producing the double chloride free from iron, and in using plant of greater capacity to make and to reduce the chloride. The process was carried out at Oldbury, near Birmingham, and brought down the cost of production to about twenty shillings per pound (44*s.* per kg.). It has also been replaced by the electrical method, and has gone out of use.

The alumina was made from alum by Webster's process.[2] The alum was mixed with tar and ignited. The mass, after ignition, was treated with hydrochloric acid to decompose any sulphides produced, then mixed with powdered wood charcoal and ignited in a retort in a current of steam and air. After this ignition the mass was lixiviated with water, potassium sulphate went into solution, and alumina remained behind.

The double chloride was made in clay retorts 10 feet long, five of which were enclosed in a reverberatory gas-fired furnace of the regenerative type; the process was similar to Deville's. Chlorine was made by Weldon's process in a neighbouring works, and led into a gasometer by earthenware pipes; it passed from this at constant pressure into the retort. Castner had a process, kept secret, for removing the chlorides of iron down to 0·01 per cent. from the double chloride, whereas originally its admixture gave the substance a pale yellow, or even dark red, colour, and caused the aluminium produced to contain as much as 5 per cent. of iron.

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[1] Würz, *Wagner's Jahresbericht*, 1882, 122.

[2] *Wagner's Jahresbericht*, 1883, p. 153.

In Castner's process sodium was made[1] from caustic soda and carbide of iron, which latter was produced by heating ferric oxide with pitch (70 parts iron to 30 of carbon). According to Roscoe the iron of this compound does not enter into the reaction, which takes place in accordance with the equation:—

$$3NaOH + C = Na\,CO_3 + 3H + Na.$$

The great advantage of this method for obtaining sodium is that the caustic soda is kept in the fused state by the action, which is not the case when ordinary soda is used. Further, if soda-ash is used, vessels of very small diameter must be employed to keep up the temperature necessary for reduction. In Castner's process egg-shaped steel vessels, 2 feet long, and 1½ feet in greatest diameter, were used for the decomposition, they held 80 lb. charges. The covers of these were fixed, while the vessels themselves, which stood on one of the movable plates closing the furnace hearth, could be moved up to the covers by hydraulic pressure, making an air-tight joint.

The vapours of sodium were led through a tube in the cover of each vessel into a special inclined cylindrical condenser, 3¼ feet long and 5 inches in diameter. The condensed sodium flowed through an opening three-quarters way down this condenser into a vessel filled to a certain height with petroleum, in which it solidified. The incondensible gases passed out at an opening at the end of the cylinder. The distillation lasted 1 or 2 hours. During this time about 7 lbs. of sodium collected in the receptacle. From 560 lbs. of soda, 67 lbs. of sodium and 540 lbs. of sodium carbonate were obtained; the latter was reconverted into caustic soda by lime. Sodium can be produced by this method at less than a shilling a pound (2 m.per kg.).

The decomposition of aluminium-sodium chloride by sodium was carried on in gas-fired reverberatory furnaces with sloping hearths

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[1] German patent, No. 40,415.

6 feet square. To 11 cwts. of double chloride 5¼ cwts. of cryolite were added, and then 350 lbs. of sodium cut into slices by a machine: the whole was then intimately mixed in drums. From this charge a little more than 1 cwt. of 99 per cent. alummium was obtained: the impurities were a few tenths per cent. of silicon and iron.

C. *Netto's Process*

This produces metallic aluminium by decomposing cryolite with sodium; the latter is obtained by reducing caustic soda with coal. It used to be practised at Wallsend, near Newcastle-on-Tyne, but has been given up.

About 200 lbs. of cryolite and 100 of salt were fused together for 1½ hours in a reverberatory furnace, and the fused mass transferred to a converter, previously warmed. Then sodium, in lumps of about 5½ lbs. weight, was pressed down to the bottom of the converter, by two workmen, with a plunger, until about 44 lbs. of sodium had been put in. The sodium decomposed the cryolite, setting aluminium free and forming sodium fluoride, which passed for the most part into a slag, a small quantity being given off as white fumes. During the action the mass, which was syrupy to begin with, became quite liquid, and aluminium collected at the bottom of the converter.

Although the specific gravity of solid cryolite is 3, and that of solid aluminium only 2·7, molten aluminium, nevertheless, sinks in molten cryolite, because cryolite expands very considerably in melting, and so becomes lighter, whereas aluminium expands very little.

The slag was poured into a special iron vessel, and then the aluminium into another, also of iron, in which it solidified. From 40 lbs. of sodium, 10 lbs. of aluminium were obtained. The slag contained 40 per cent. of sodium fluoride, 43 per cent. of sodium chloride, 15 per cent. of cryolite, 0·75 per cent. of metallic aluminium and a small quantity of alumina. If a metal free from iron and silicon was desired, the sodium added was only one-third of that necessary to decompose the cryolite. Then iron and silicon were reduced at the same time as aluminium and taken up by the metal. The fused mass was separated from these metals by pouring it into a second converter, where metal with 98 to 99 per cent. of aluminium was obtained by the further addition of sodium.

The 0·75 per cent. of the metal in the slag was removed by copper, and formed aluminium bronze. The slag was then worked up into cryolite and Glauber's salt, by the addition of aluminium sulphate. The following reaction took place:—

$$12NaF + Al_2(SO_4)_3 = Al_2F_6,6NaF + 3Na_2SO_4.$$

The sodium sulphate was washed out of the fused mass, and cryolite remained as residue.

To make the sodium, Netto allowed fused caustic soda to drop on a layer of red-hot coke which was at the bottom of an upright cylindrical retort of cast-iron or cast-steel, covered by a jacket of clay. Part of the soda was reduced to sodium in the state of vapour, the remainder forming sodium carbonate. The vapours of sodium were condensed in receivers attached to the upper part of the retort, and collected in a vessel containing oil. The sodium carbonate in a fluid state collected at the bottom of the retort and was removed from time to time. To produce 1 lb. of sodium and 9 lbs. of soda slag containing 60 per cent. carbonate, required 6 lbs. of caustic soda, 12 of coke, 1½ of wood charcoal, the retort consumption being equal to 1·2 lbs. of cast-iron.

This process of Netto, carefully thought out as described, cannot possibly compete with the electrolytic method.

D. *Grabau's Process*[1]

This consists in decomposing aluminium fluoride (Al_2F_6) with sodium according to the equation:—

$$2Al_2F_6 + 6Na = 2Al + Al_2F_6,6,NaF.$$

Thus besides the metal an artificial cryolite is obtained which is used to make aluminium fluoride. This is made from aluminium sulphate, cryolite and fluorspar. A solution of aluminium sulphate ($Al_2(SO_4)_3$) is warmed with powdered fluorspar, and thus gypsum is formed by part of the sulphuric acid with its equivalent quantity of calcium, while the other part is united with the fluorspar forming an aluminium sulphate and fluoride. This takes place according to the following equation:—

$$Al_2(SO_4)_3 + 2CaF_2 = Al_2F_4SO_4 + 2CaSO_4.$$

The solution is evaporated down to a pasty consistency after separating the gypsum and undecomposed fluorspar, and then mixed with enough cryolite to enable the whole of the sulphuric acid to combine with the sodium:—

$$3Al_2F_4SO_4 + Al_2F_6.6NaF = 4Al_2F_6 + 3Na_2SO_4.$$

After drying and igniting the whole, the sodium sulphate is washed out and the residue of aluminium fluoride is ready for the metallurgical process. This compound is therefore continually regenerated, while new supplies of aluminium sulphate, fluorspar, and sodium are needed.

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[1] German patents, Nos. 47,031, 48,535, 51,898.

At the beginning native cryolite must be used instead of the artificial compound yielded in the process, although this mineral is always rendered impure by spathic iron ore and silica. The aluminium fluoride is heated before the process begins, but not to fusion; the sodium is fused beforehand.

The arrangements for carrying out this process are to be seen in Figs. 346 and 347.[1] *x* and *y* are vessels for the heating of the substances used. They are made of cast-iron and lined with burnt fire-clay. In *x* the aluminium fluoride is warmed, in *y* the sodium is melted. *x* is closed by a sliding piece *v* at its lower end, *y* has a stopcock *t*. *R* is the fire-place, *Z*, *Z* are the flues, *W* the lower part of the chimney. *M* is the vessel for the reduction, hung on trunnions. It is formed of hollow iron walls cooled by water which passes in and out by the tubes *g*, *g*. *N* is the vessel which receives the molten mass after the action, and is likewise jacketed with water which flows in and out at *g′*, *g′*.

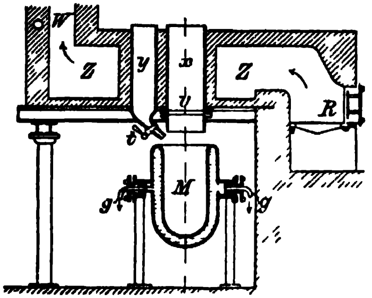

FIG. 346

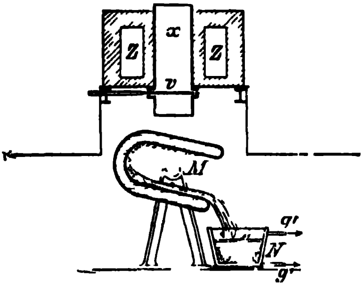

FIG. 347

When the process is started, *x* is filled with aluminium fluoride (or cryolite if it is an initial process) and *y* with sodium. When the fluoride is red-hot (which will be known by its giving off white fumes), the sodium is tapped by turning the stop-cock *t* into the vessel *M*. Then the slide *v* is drawn out and the powdered fluoride falls also into the vessel, where it collects upon and covers the molten sodium. The action which at once begins, disengages so much heat that the fluoride is melted. The length of time needed is only some seconds. Aluminium collects at the bottom of the pot. This is tipped up and its fluid contents emptied into the receiver *N*.

In this method more than 90 per cent. of the sodium is made use of. It is made electrolytically from common salt, and chlorine obtained as a by-product.[1]

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[1] Dammer, *Chem. Technologie.* Vol. ii. (*Metallurgie*), p. 217.

The process has not been an economic success, in spite of the fact that it is well thought out, and is the best of all those for which sodium is necessary, on account of the low cost of production of that metal.

Beketoff[2] used magnesium instead of sodium for the extraction of aluminium from cryolite. This process was carried on for some time in certain works, *e.g.* in Hemelingen, but has been abandoned.

2. THE ELECTROMETALLURGICAL PRODUCTION OF ALUMINIUM

This has not been possible hitherto with aqueous solutions, for only hydrates of alumina are obtained by the electrolysis of solutions of its salts in water, or i. any solvent containing hydrogen and oxygen.

In the present state of technological knowledge, aluminium must be obtained by electrolysing fused compounds. The first experiment of the kind was made by Bunsen and Deville in 1854.

Bunsen decomposed aluminium-sodium chloride, fused at 200°C., in a porcelain crucible. This was divided into two parts by a porcelain partition extending nearly to the bottom, and each part contained a carbon electrode The carbon plate forming the anode was plain, but that forming the cathode was concave and had horizontal saw-like depressions in which the molten metal collected. At a low temperature aluminium separated as powder. To avoid this undesirable result the temperature was raised to that of the melting point of silver, and common salt was introduced into the crucible.

Buttons of aluminium were then obtained in these depressions, they were put into strongly heated molten salt, where they united.

Deville decomposed the double chloride of aluminium and sodium similarly, using however a platinum cathode instead of carbon. His apparatus is shown in Fig. 348.[3]

H is a Hessian crucible in which is placed a porcelain one *P*. *D*. is the cover, through which passes the cathode *K*, a strip of platinum. The cover is also pierced by a porous clay cell *R*, which contains the anode *A*, a piece of gas-coke, hanging in it. The crucible and the porous cell were filled to the same level with the fused double chloride, and then the current was passed. Aluminium mixed with salt formed a deposit on the cathode, and was removed from time to time by lifting the strip of platinum out of the crucible. The mixture of metal and salt was remelted and a button obtained.

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[1] German patent, No. 51,898, 8 Oct., 1889.

[2] *Jahresbericht der Chemie*, 1865.

[3] Borchers, *Elektrometallurgie*, p. 114.

Attempts to manufacture aluminium upon these lines were beset by insuperable obstacles. No material could be found suitable for making vessels for fusing and electrolysing, for all that were tried were acted on by the fused haloid salts, or by the metal itself, at the high temperature, and impure aluminium resulted.[1] Crucibles of siliceous material caused silicon to pass into the aluminium. Clay and graphite were attacked by the double chloride. Compressed coke crucibles were so porous that they could not be heated unless surrounded by thick jackets. Metals could not stand the temperature, they were attacked by their molten contents, and thus alloyed with the aluminium. Further, carbon was not suitable as the cathode material. According to Borchers[2] the cohesion of the particles of carbon, in the cathode and crucible, was so loosened by the penetration of the metal into the pores that it appeared as though in a state of fusion.

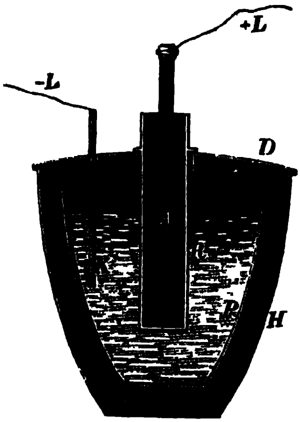

FIG. 348

Thus we find that none of those electrolytic processes were successful that depended on heating vessels from outside while they contained aluminium compounds to be electrolysed in the fused state. They can now be passed over. The one thing to be done to make a process possible was to generate the heat within the vessels, by means of an electric current. (Very recently, a proposal has been made to electrolyse aluminium sulphide, dissolved in potassium or sodium chloride, and fused by external heat: it appears that electrolysis is thus possible.)

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[1] Borchers, *Elektrometallurgie*, p. 115.

[2] Borchers, *loc. cit.*

The production of heat by the current itself may be effected by allowing an electric arc to be formed within the containing vessels, or by placing the materials to be fused and decomposed as resisting media in the circuit. The latter method has proved far more profitable than producing an electric arc. This, even when weak, has a far higher temperature than is necessary to fuse and keep liquid aluminium compounds, so that a great part of the heat produced is wasted. Further, its effect is concentrated into so small a space that it becomes difficult to heat a large quantity of the aluminium compound at all evenly.

These objections do not apply to the generation of heat by the resistance of aluminium compounds in the circuit. The heat developed by the resistance of these in the fused condition is great enough to fuse, and keep liquid, substances of high melting point, if a suitable current is employed. Moreover the electrolyte will become heated uniformly, even though the electrodes dipping into the fused material possess a smaller area than the section of the cell. This second method of heating is consequently chiefly employed at present.

It was first applied to the production of alloys of aluminium from its fused compounds, and so used by the brothers Cowles as early as 1884, and in 1887 by Héroult.

Cowles Brothers led the current through a mixture of alumina and coal, while Héroult melted alumina alone and electrolysed it, without coal. In both cases aluminium was separated and alloyed with copper.

Cowles' process is described under Aluminium Alloys. It has led, as already stated, to a diversity of opinion as to whether the action of the current is purely electrothermic or also electrolytic: whether alumina is decomposed by the carbon with which it is mixed, or split up into aluminium and oxygen by the current. The inventor himself considers that neither of these processes takes place exactly, but that the alumina dissociates at the high temperature, and that the dissociation is assisted and rendered permanent by the carbon present.

In Héroult's process, in which carbon anodes are used, with fused metal cathodes (which alloy themselves with aluminium), an undoubted electrolytic decomposition of the alumina must take place, the compound being first fused by the current. In his description of his patent he lays stress on the electrolytic action.[1]

Although Héroult's apparatus is used only for the production of alloys it certainly led the way for the preparation of pure aluminium; it therefore deserves a full description here. Its arrangement is shown in Figs. 349, 350.[2]

The vessel in which the fusion and decomposition take place is a cast-iron box, which is provided with a strong lining of carbon plates These are cemented together by tar, syrup or lævulose. To bring this lining into contact as close as possible with the iron, the latter is cast round it. When cooled the metal firmly adheres to the lining. The box itself is made the negative terminal by the copper screw *a*. The positive terminal consists of a series of carbon plates

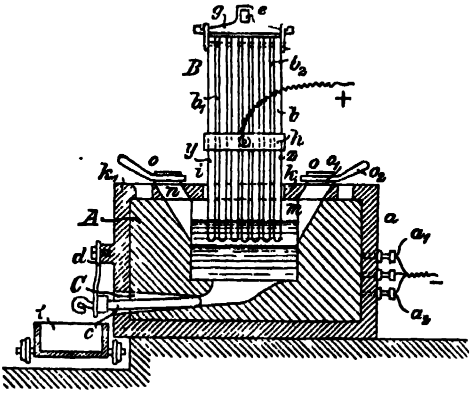

FIG. 349.

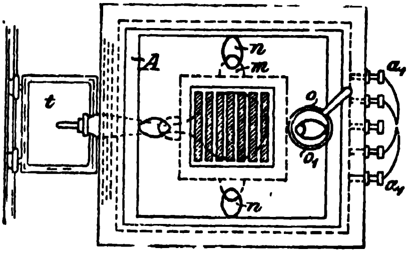

FIG. 350.

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[1] French Patent, No. 170,003, April 15, 1887; Belgian Patent, No. 77,100, April 16, 1887; English Patent, No. 7426, May 21, 1887; German Patent, No. 47,165, Dec. 8, 1887; United States Patent, No. 387,876, Aug. 14, 1888.

[2] *Schweizer Bauzeitung*, 1888, 28.

b, b_1, b_2, etc., which dip into the vessel. These plates are either firmly attached to each other, or the spaces left between them are filled with a conducting body, copper or light coal. At the upper end they are held together by the framework *g*, at the middle by the framework *h*. The former has an eye *e* to which a chain can be fastened, and by which the electrode can be put into position and raised and lowered at will. The current is led to the framework *h*.

The box is closed at the top by graphite plates, in which are various openings, *i*, *n*, *m*; *i* is the space to admit the anode, *n* and *m* are openings for charging and to let out gases. These have plates for covers (*o* and o_1) provided with handles. The space between the upper edges of the box and the graphite top is filled with powdered wood charcoal. A taphole *c* enters the box at the deepest part of the bottom, and through this the aluminium alloy is tapped into the mould *t*, lined with charcoal, which produces the alloy in the form of a rectangular block. The taphole *c* is closed with a stick of charcoal *e* provided with a handle *d*.

The working is as follows: Finely divided copper is sprinkled on the bottom of the vessel, the anode is dropped in, the circuit closed, and the copper melted by the electric arc The alumina is placed on top of this copper, which now acts as the cathode. The alumina melts, becomes a conductor, and is consequently split up by the current into aluminium and oxygen. The former passes into the copper and forms aluminium bronze, while oxygen goes to the anode and forms carbon monoxide with the carbon. This gas passes away through the openings. The alloy is tapped out from time to time, and the anode at the same time lifted out, while copper and alumina are added when necessary. The anode can be raised or lowered according to the resistance wanted.

The current used is 13,000 ampères working with a difference of potential of 12 to 15 volts.

The quantities of aluminium separating from the alumina during the process appear to correspond to the formulas Al_6O_3, Al_4O_3, or AlO. Therefore if the process is merely electrolytic it must be assumed that at the temperature at which the action takes place (a bluish-white heat), aluminium is combined with a smaller proportion of oxygen than it is in alumina.

Pure aluminium has been made recently with a similar apparatus by using a suitable solvent for alumina, a specially adapted electrolyte, and a suitable cathode.

The materials used have been aluminium oxide dissolved in molten chlorides of the alkalies or alkaline earths, or in aluminium chloride itself; molten mixtures of aluminium fluoride or oxyfluoride with alkaline carbonates, and also aluminium sulphide dissolved in alkaline chlorides.

At present the exact method of producing aluminium on the large scale, as well as the apparatus and the economic results, are kept entirely secret. The author has therefore been compelled to rely only upon data obtained from technical literature and the patent publications, and to select his material most carefully.

A. *Production of Aluminium from Solutions of Alumina in Haloid Salts of the Alkalies, or of the Alkaline Earths, or of Aluminium itself.*

This process is carried on like Héroult's, already described. Alumina is liquefied by the action of the current, and dissolves in the molten chlorides. It is then decomposed by the current into aluminium and oxygen. Aluminium collects on the cooled metal forming the cathode, and oxygen forms carbon monoxide with the carbon of the anode. As the aluminium collects, fresh alumina is added.

To obtain pure metal it is necessary to begin with pure alumina. This is generally obtained from bauxite, which always contains ferric oxide and silica. It is ignited with soda, and the sodium aluminate leached out with water, which leaves these and other impurities behind in the residue. By leading carbon dioxide through the solution, aluminium hydrate is precipitated and sodium carbonate formed again in the solution. The hydrate is converted into alumina by heating.

Alumina can also be obtained by heating aluminium sulphate until the sulphuric acid has been completely driven off.

Borchers[1] describes the following apparatus for making pure aluminium in the method stated above. The vessels are flat iron cylinders, open above, with linings of some difficultly fusible and pure aluminium compound. The anodes are carbon plates fastened together, the cathodes are of metal passing through the bottom of the vessel, and easily kept cool. The walls of the vessel are cooled in order that the lining shall not be attacked. The process is continuous, as the whole amount of aluminium present is kept constant by the regular addition of alumina as the metal separates. A very strong current is necessary to fuse the alumina and keep it liquid (about 2,300 ampères per square foot of cathode surface). The temperature of the electrolyte is not allowed to rise higher than necessary, so as to prevent the aluminium being oxidised to some lower oxide and passing back into the solution, and also to prevent the reduction and volatilisation of the alkali metals.

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[1] *Elektrometallurgie*, p. 153.

The apparatus in Fig. 351 is one described by Borchers[1] and used for experimental purposes, in which it gave good results. *T* is

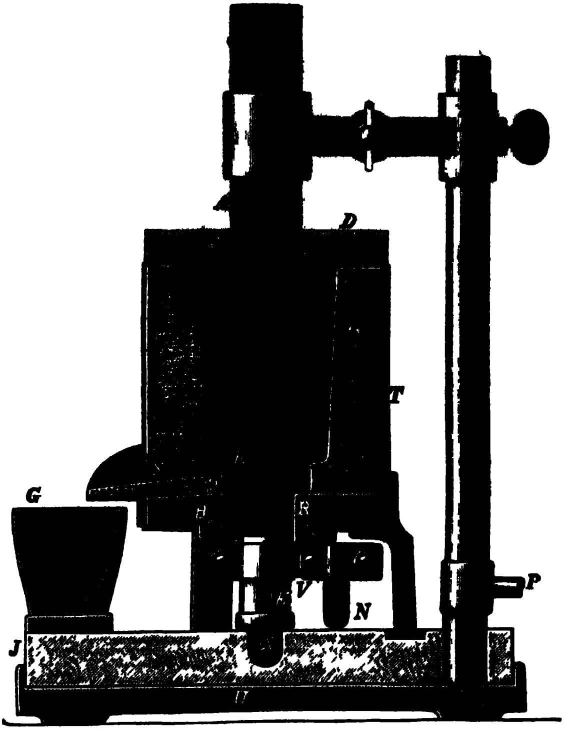

FIG 351.

the cylindrical vessel for fusing and electrolysing. The sides are made of iron, the bottom of powdered clay. *F* is the lining composed of alumina or some specially infusible aluminium compound. The cathode is the steel plate *K*, in the lining of the bottom. This is protected from fusion by the cooling tube of copper *R* in which water circulates; it is screwed up to the plate. Cold water enters at the tube *E*, ascends in *R*, passes into the tube *X* and out at the bottom, warmed. The negative terminal *N* is clamped to *R* by the screw *V*, *R* being in good connection with the steel plate *K*. *A* is the anode, made of carbon. It is attached by an iron clamp to an iron rod screwed tight into an iron plate *U*. The current enters by the copper rod *P* which is attached to the iron rod with a copper socket. The vessel is insulated from this by the fireclay layer *J*. The aluminium is tapped out from time to time through the hole *S* into the mould *G*, while gases formed in the process escape through openings made in the cover *D*.

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[1] Borchers, p. 147, Fig. 86.

The lining of the apparatus is not attacked, as it is kept cool by the walls being in contact with the air. If there is a lengthy experiment with strong current the walls are further cooled by water, and freezing materials laid round the vessel or introduced into the lining.

In charging the apparatus a small quantity of aluminium is first placed on the bottom and then fused by letting the anode approach the cathode; this aluminium now forms the cathode. The electrolytes are now introduced. These fuse and form a liquid layer separating the two electrodes, and aluminium and oxygen are generated in the layer. As the alumina is used up more is added with a corresponding amount of solvent.

Fig. 352[1] shows an apparatus described by Kiliani,[2] with an anode which can be rotated. The vessel *b*, for fusing and electrolysing, is carried on pillars *a*, *e* is the anode attached to a spindle *f*. The spindle has annular teeth which fit into the toothed-wheel *g*. This can be moved by the hand-wheel h^2 and the spiral screw $h\,h^1$, and the anode thus raised or lowered. The rotating of the anode is effected by the spiral screw *i* and the corresponding wheel *k* keyed on to the spindle. The positive current flows through brushes into the spindle and thence to the anode, while the rod *c* forms the negative connection. During electrolysis the anode is quickly rotated in the electrolyte into which it dips. No information is given about the lining of the vessel, or the metallic pole serving as cathode.

Charles Hall's[3] process consists in subjecting a solution of alumina in molten cryolite to electrolysis. Hall concludes that the alumina is electrolysed, as the fluorides remain unaltered.[4] The details of the process are secret. It is not known how far the process was actually carried out in accordance with the directions given in the various letters patent.[5] These documents have undergone an exhaustive criticism by Borchers.[1] It is a fact that the process has been adopted by the Pittsburg Reduction Company, and that in 1894 this Company produced aluminium at the rate of one ton per day.[2] The Company proposes to utilise 6,500 electric horse-power from Niagara Falls to prepare aluminium in this way.

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[1] Borchers, p. 149. [2] German Patent, No. 50,508, April 21, 1889.

[3] *Mineral Industry*, 1893, p. 7.

[4] *Journal of the Frankland Inst.*, vol. 98, 319, 391.

[5] American Patents, Nos. 400,766, 400,664, April 2, 1889, and Nos. 400,665, 400,666, 400,667.

According to recent statements by Dr. Charles Hahn,[3] a fused mixture of cryolite, fluorspar and aluminium fluoride is used as the solvent, dissolved alumina being the electrolyte. The vessel is of cast-iron lined with charcoal. The cathode is of carbon, the anode copper or platinum. The charge of alumina is 10 to 12 lbs. The mixture fuses and remains liquid with no other source of heat than the current. A potential of 5 volts is enough to overcome the internal resistance and electrolyse the alumina when external heat is applied to fuse and keep the mass in the molten state.

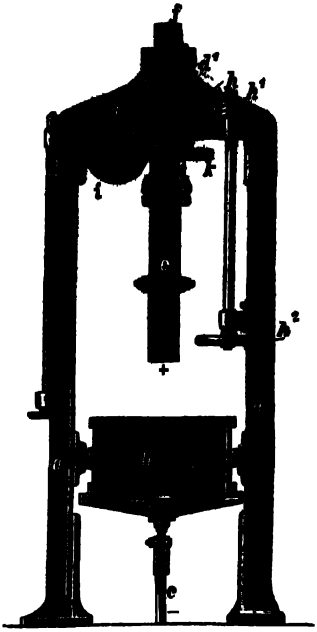

FIG. 352.

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[1] *Elektrometallurgie*, p. 136. [2] *Mineral Industry*, 1893, p. 7.

[3] *Elektrometallurgie des Aluminiums in Amerika*, *Zeitschr. f. Elektrotechnik*, 1st Sept. 1895, p. 478.

This process seems to yield 50 per cent. aluminium out of alumina containing 53 per cent.

A process suggested by Joseph B. Hall[1] electrolyses alumina in a bath of aluminium chloride with sodium and lithium chlorides. The electrolyte is supplied by the anode, which consists of a mixture of alumina and charcoal. When the circuit is closed the alumina in the anode passes gradually into the liquid and is there decomposed. The oxygen set free seems to oxidise the carbon of the anode to monoxide. The cell is a vessel made of carbon or a mixture of alumina and carbon with an outer shell of iron: the separated metal collects on the bottom and can be removed from time to time by tapping.

Experiments made with this process seem to have been satisfactory.

Minet's process is to electrolyse a liquid containing aluminium fluoride as single or double salt, and to renew this with alumina or with bauxite. He is of the opinion that the fluoride is the real electrolyte, and that the fluorine set free acts upon alumina to form more of this salt, so that the liquid remains unaltered. The first experiments in this method were made at Creil, Department of Oise, France, where a fused mixture of 40 per cent. cryolite and 60 per cent. salt was electrolysed and the liquid renewed by alumina or bauxite.

Aluminium sodium chloride, Al_2Cl_6 $2NaCl$ was also experimented on, but proved too volatile, while the double fluoride volatilised only slightly at the temperature necessary (800°–1000°C.) and maintained a convenient degree of fluidity.

This method cannot be criticised as the details are kept secret. Such as are given in the letters patent[2] have been exhaustively criticised by Borchers.[3]

A process is said to be in use at Ste. Michel, in Savoy, where 6,000 h. p. out of an available water power supply of 30,000 appear at present to be used. A vessel lined with carbon forms the negative electrode. A thin covering of aluminium seems to form on the surface of this lining and protect it from rapid action; it is said to last 20 to 30 days. The liquid is renewed at stated times with a charge consisting of 48·2 parts of aluminium hydrate containing water, 24·3 parts of cryolite, 27·5 parts of aluminium oxyfluoride, with corresponding quantities of common salt.[4]

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[1] *Engineering and Mining Journal*, 1895, p. 581.

[2] English Patent, No. 10,057, 1887.

[3] *Elektrometallurgie*, p. 142.

[4] *Oesterr. Zeitschr. f., Berg. und Hütt.*, 1893, p. 491.

According to Minet,[1] the strength of current should be 1,500 ampères, the potential 4·55 volts. To obtain a kilogram of aluminium per hour 30·3 h. p. should be necessary. But since there is a loss of 12 per cent. of energy in converting mechanical into electrical energy, this h. p. is equal not to 736 watts but to 650 watts; consequently 35·4 h. p. should be necessary for 1 kg. of aluminium per hour. According to these numbers, 1 h. p. per hour should yield 28·2 grammes of aluminium.

Brand[2] calculated that in this case only 58 per cent. of the energy supplied is utilised. According to Faraday's formula 0·337 grammes of aluminium should be obtained by a current of 1 ampère in an hour. Thus by theory there is necessary to produce 1 kg of aluminium in 1 hour,

$$4{\cdot}55 \text{ volt} \times \frac{1000}{0{\cdot}337} \text{ amp.} = 4{\cdot}55 \text{ volt} \times 2967{\cdot}4 \text{ ampères.}$$

But in practice 650 watts × 35·4 h. p. are necessary. Therefore the fraction of this energy utilised is—

$$\frac{4{\cdot}55 \times 2967{\cdot}4}{650 \times 35{\cdot}4 \text{ h.p.}} = 0{\cdot}58$$

According to Hampe this waste is chiefly due to the fact that part of the aluminium while in the nascent state is dissolved by the fluorides.

Borchers[3] assumes as the result of his experiments that the electrolysis of alumina in solution in haloid salts requires a potential of 9 to 10 volts, and a current of 2,300 ampères per square foot cathode surface, and that $\frac{3}{8}$ kg of metal is set free for every 24 electric h. p. per hour.

Taking the direct electrolysis of alumina, and the statement that in Neuhausen 20 grams aluminium were obtained with 1 h. p. (650 watts) per hour, Brand[4] calculates the utilised energy as 13·4 per cent. The remaining 86·6 per cent. seems to be chiefly converted into heat by the resistance in the circuit.

The Kleiner-Fiertz[5] process makes use of an electric arc to fuse and decompose an alkaline double fluoride of aluminium in which alumina is dissolved. The vessel containing the fused electrolyte is lined with bauxite or clay. The arrangement is to be seen in Figs. 353, 354.[1] *B* is the vessel, filled with molten cryolite, and lined with bauxite or clay. *A* is the anode, *K* the cathode; both are movable. The motion of the anode is regulated by a loaded lever and a solenoid, the latter being connected with a piston dipping into a liquid and limiting its motion. When the current passes aluminium is deposited on the negative electrode. The electrolyte is renewed by taking alumina from the lining of the vessel.

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[1] *Comptes Rendus*, 110, 1890; 342, 1890; 231, 1215, 1891.

[2] Dammer, *Chem. Techn.*, vol. iv., p. 225.

[3] *Elektrometallurgie*, p, 152.

[4] *Chem. Techn.*, *loc. cit.*

[5] German Patent, No. 42,022, 1886.

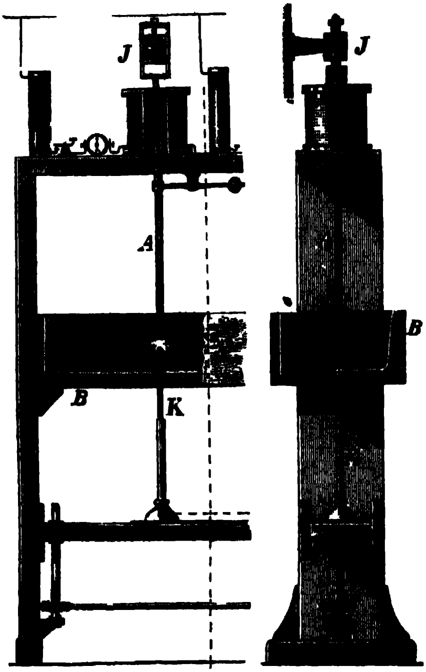

FIG. 353.

It has been already stated that the use of the electric arc is costly, and that its effect is contracted into a small space. The molten material easily forms crusts in contact with the cold material, so that it is very difficult to ensure a regular action.

This method has therefore not come into definite use.

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[1] Borchers, *l. c.*, p. 129.

B. *Preparation of Aluminium from a Fused Mixture of Aluminium Fluoride or Oxyfluoride with Alkaline Carbonates*

Grabau[1] subjects to electrolysis a fused mixture of the fluoride (or oxyfluoride) with soda or potash, and obtains besides aluminium an alkaline fluoride, or else cryolite. The fusion and electrolysis are performed by the aid of the electric arc. Cryolite is first fused in the vessel, and then a mixture of aluminium fluoride and soda introduced. The anode is carbon, the cathode a metal, preferably aluminium. During electrolysis the metal separates at the cathode and carbon dioxide is set free at the anode. This comes partly from the molten material oxidising the anode, and partly from the action of the aluminium fluoride on the soda. Instead of the fluoride, the oxyfluoride is sometimes used, as it is easily prepared.

The proportion in which either of these is mixed with the alkaline carbonate depends upon whether sodium fluoride or cryolite is desired as a by-product. When the fluoride is employed, and sodium fluoride formed, the action is as follows:—

$$2\ Al_2F_6+6\ Na_2CO_3+3\ C\ (\text{Anode})=4\ Al+12\ NaF+9\ CO_2,$$

but if cryolite is to be the by-product the action must be:—

$$4\ Al_2F_6+6\ Na_2CO_3+3\ C=4\ Al+2(Al_2F_6.\ 6\ NaF)+9\ CO_2.$$

When the oxyfluoride is used, and sodium fluoride is to be the secondary product, the action should be according to the equation:—

$$2\ Al_2OF_4+4\ Na_2CO_3+3\ C=4\ Al+8\ NaF+7\ CO_2,$$

while to give cryolite the action should be:—

$$3\ Al_2OF_4+3Na_2CO_3+3\ C=4\ Al+Al_2F_6.\ 6\ NaF+6\ CO_2.$$

Borchers[2] considers it probable that the lively evolution of carbonic acid noticed when the mixture of aluminium fluorides and alkaline carbonates is fused, takes place according to this equation:—

$$Al_2F_6+3\ Na_2CO_3=Al_2O_3+6\ NaF+3CO_2.$$

According to this the electrolyte is oxide of aluminium dissolved in alkaline fluorides.

The advantages of this process are the purity of the aluminium, as the material is easily prepared free from iron and silica, and the production of cryolite as a by-product.

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[1] German Patent, No. 62,851, 1891.

[2] *Elektrometallurgie*, p. 150.

According to Borchers[1] the employment of the electric arc is subject to the same drawbacks as stated for the Kleiner-Fiertz process.

The process, which answers well on a small scale, is reported to be used at Trotha near Halle. Up to the present no aluminium has been sent from there into the market.

To obtain pure aluminium fluoride, which is absolutely necessary for pure aluminium, as well as to obtain it merely free from iron, Grabau has devised special processes.

To make the pure compound,[2] powdered calcined clay, as free as possible from iron, is taken, and treated in slight excess with hydrofluoric acid of 12 per cent. strength, or with correspondingly stronger hydrofluosilicic acid. When hydrofluoric acid is used, the temperature must be kept down to 95°, but if the other acid is used, the action must be assisted by heating.

The mass becomes neutral in a few minutes, after which the liquid, consisting of aluminium fluoride, is filtered at a medium temperature from the residue, which is hydrated silica and undecomposed clay. The residue is washed with hot water, which removes any aluminium fluoride remaining. In this way 90 per cent. of the hydrofluoric acid added seems to be used to form the aluminium fluoride.[3]

To obtain this fluoride merely free from iron,[4] a solution of it is treated first with sulphuretted hydrogen to remove lead, arsenic, and other metals, and to reduce ferric salts present to ferrous. This reduction is necessary, as otherwise ferric fluoride is found in the crystals of aluminium fluoride obtained. The liquid, filtered from the residue, is acidified to prevent the precipitation of traces of iron sulphide in the cooling which follows, and then cooled in vessels made of sheet aluminium. Here hydrated crystals of aluminium fluoride separate out ($Al_2F_6.18H_2O$). The crystallisation is concluded as soon as the temperature, which rose at the beginning, has been brought down to 0° by continued cooling. The whole is separated into mother liquor and crystals in centrifugal pans, and the crystals are washed with ice-cold water.

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[1] *Elektrometallurgie*, p. 130.

[2] German Patent, No. 69,791.

[3] German Patent, No. 70,155.

[4] *Zeitschr. für Angew. Chemie.*, 1893, p. 462.

C. *Preparation of Aluminium from Fused Mixtures of Aluminium Sulphide and Alkaline Chlorides*

The preparation of the metal from its sulphide is said to be practised at the present time at Neuhausen in Switzerland, and has been proposed by Bucherer in Cleveland, and also by the Aluminium-Industrie-Actien-Gesellschaft in Neuhausen.

Bucherer, in Cleveland, Ohio, U.S.A.,[1] uses aluminium sulphide in the form of double sulphide with an alkali or alkaline earth. This is subjected to electrolysis in a bath of molten chloride or fluoride of alkali or alkaline earth, or of a mixture of them. Sodium or potassium chloride, or the two mixed, is found to be the best solvent. The double sulphide is made more cheaply and easily than aluminium sulphide alone and yields a pure metal when electrolysed aluminium being separated at the cathode by a current of low potential.

The double sulphide is prepared by Bucherer, by heating aluminium oxide or hydrate with the sulphide or polysulphide of an alkali or alkaline earth, and excess of sulphur and coal. The action is as follows:—

$$3Na_2S + Al_2O_3 + 3C + 3S = Na_6Al_2S_6 + 3CO.$$

He proposes to make pure aluminium sulphide by the slow action of sulphur vapour on a mixture of alumina and coal heated to white heat in a clay retort. The action would then be:—

$$Al_2O_3 + 3C + 3S = 3CO + Al_2S_3.$$

The process of the Aluminium-Industrie Co., in Neuhausen,[2] consists in electrolysing the sulphide Al_2S_3 alone or in a bath of alkaline or alkaline-earthy chloride, or fluoride. The electrolyte may be fused and maintained liquid with the help of external heat, or by the current alone. If the solution of aluminium sulphide in sodium or potassium chloride is first fused in a vessel heated from without, and then kept fluid during the electrolysis, a current with a potential of 2·5 to 3 volts will be enough to electrolyse the sulphide, but if the solution is fused and kept fluid by the current alone, a potential of 5 volts will be necessary.

The process seems to be best carried on in a vessel of cast or wrought iron, which is lined with charcoal. Aluminium appears at the cathode, sulphur at the anode. The liquid itself generally prevents the oxidation of the sulphide; if it is desired to secure this further, reducing gases are passed over the fused mass.

---

[1] German Patent, No. 63,995, Nov. 18, 1890.

[2] German Patent, No. 68,909.

In this process the lining of the vessel is not attacked, nor the carbon electrodes dipping into the molten electrolyte, because the temperature of the bath is not high enough for the sulphur set free to combine with carbon. Consequently the aluminium is very pure.

Further advantages in the method may be pointed out:—the comparatively small strength of current needed, the prevention of short circuiting, as aluminium is heavier than the liquid, and sinks quickly to the bottom, and the possibility of collecting the sulphur fumes at the anode, and utilising them.

The details of the process are secret.

The works at Neuhausen now turn out 2 tons of aluminium daily with the use of 5,000 h.p. The process by means of direct reduction of alumina seems to have been given up.

Borchers' objection to the method is that the preparation of the sulphide as performed at present is too costly, for it requires pure alumina which can itself be directly electrolysed to give aluminium. Further, its production by heating alumina, charcoal and sulphur requires a great consumption of fuel.

With a considerable lowering in the cost of production of aluminium sulphide, its electrolysis would prove the best process of all to obtain aluminium.

3. PREPARATION OF ALUMINIUM ALLOYS

The process of Cowles Brothers and that of Héroult were used on the large scale to prepare the alloys directly until a short time ago. But since we are now able to produce aluminium itself electrometallurgically in large quantity, these original processes are not so much used, as it is more economical to make the alloys by fusing aluminium with the necessary metal.

A. *The Cowles Brothers' Process*[1]

is used in Cleveland, Ohio, U.S.A., and was published in 1884. It consists in extracting aluminium from a mixture of alumina and charcoal by an electric current, and alloying this with another metal the moment it is reduced. The current produces the heat necessary to reduce aluminium, because of the resistance of the mixture of alumina and charcoal. We have already referred to the different views taken as to the real nature of the action. Borchers believes that the high temperature causes the alumina and carbon to react, others believe that the current electrolyses alumina into its elements. Cowles Brothers do not agree with either view, but hold that the high temperature dissociates alumina into its elements.

---

[1] United States Patent, No. 319795.

The arrangement of the Cowles apparatus is shown in Figs 355 and 356.[1] Fig 355 is a longitudinal and Fig. 356 a transverse section.

The furnace consists of a box of rectangular section with walls and hearth made of fireclay. E, E are the electrodes These are bundles of carbon pencils, usually 9, about 1¼ inch thick, which are placed in metallic cylindrical cases, M, cast round them. These consist of iron or copper according to the alloy desired At the head of each case is a copper rod *K*, making connection with the conductor *L* through the copper clamp *V*, to which is clamped on one side the conically pointed end of the copper rod, and to the other, the end of the wire *L*. *R* represents the inclined

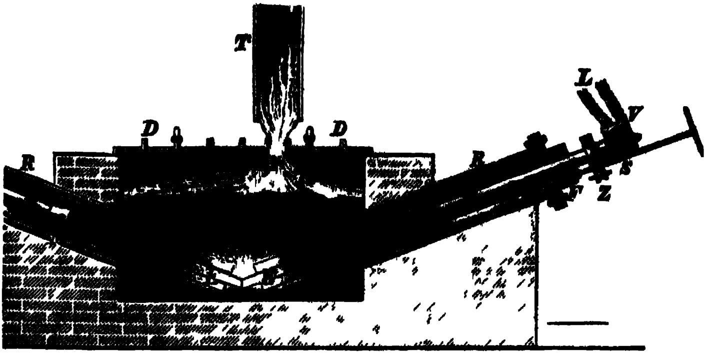

FIG. 355

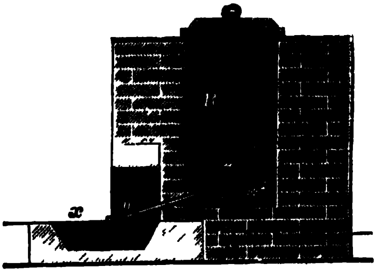

FIG. 356

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[1] Borchers, *Elektrometallurgie*, p. 102; *Industries*, vol. cxv., 1888, p. 237.

cast-iron tubes, in which the electrodes may be moved forwards or backwards, by the screws *S*. The carbon pencils act as resistance to the current, become red-hot, and communicate their heat to the charcoal, alumina and metal around them. *D* is the cover of the apparatus, made of cast-iron. The opening *Y* in this allows the carbon monoxide gas formed by the oxidation of the charcoal to pass into the tube *T*, which is in communication with a condensing chamber to arrest any alumina carried off by it. *O* is the tap-hole to let the molten alloy out into the receiver *X*.

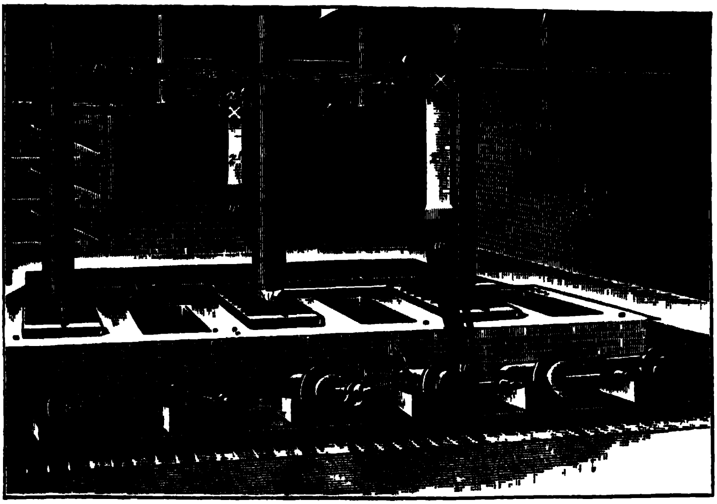

FIG. 356.

A furnace is about 5 feet long; they are built in a block as is shown in Fig. 357.[1] This shows part of the plant of the "Cowles Syndicate Co," which has now been disused for a long time. The current was produced by a Crompton Dynamo Machine of 40 h. p.; it had a potential of 60 volts and a strength of 6,000 amp.

The current was conducted by copper wires to the copper rods *k* and *k* which ran respectively along the front and back of the furnaces. The wires were attached to the rods by copper clamps *z*. The upper ends of these had pulleys which ran on the copper rods. From their lower ends ran a bundle of copper wires, *w*, which in their turn were connected with copper rods in the way shown in the figure.

---

[1] *Industries*, *l.c.*: Borchers, *l.c.*, p. 100.

Only one furnace was worked at once, the others were meanwhile being cooled, charged or emptied. The operations took place as follows: First, a layer of wood charcoal to the depth of a hand was spread out on the bottom of the furnace. This is previously soaked in milk of lime and dried to prevent its agglomeration. Then the electrodes were put in place. Next a frame made of iron plate is introduced, and the space within it filled with a mixture of alumina (bauxite, corundum or emery). wood charcoal and the metal with which the alloy is to be made. These substances are all finely divided. (The metal is sometimes not finely divided but in the form of rods which are arranged in the furnace either cross-wise, or perpendicular to the long axis.) The space between this iron frame and the side walls of the oven is filled with a lining of wood charcoal, after which the frame is removed. A conductor for the current through the furnace is then formed by arranging pieces of retort carbon, and any space remaining is filled with wood charcoal; the cover is next put on, and the current started. The beginning of the reduction of alumina is signalled by the appearance of a white smoke. The aluminium which separates forms an alloy with the molten metal which has been put in; this collects at the bottom of the furnace, and is tapped out at the end of the operation. Besides this alloy a sort of slag is formed which is an intimate mixture of the alloy with charcoal. This is powdered and washed, and the portions containing metal are added to another charge. Carbon monoxide is formed from the oxygen of alumina and the charcoal. It passes through an opening in the cover, and through a condenser as already explained.

The end of the process is known by the cessation of the white smoke. The smelting lasts about one hour. The furnace is thrown out of circuit, and the current at once turned on in another one. The amount of aluminium in the alloy is 15 to 35 per cent. This may be converted into any other percentage by melting it with aluminium or the other metal, or any new metal as desired. So, for example, aluminium bronze is obtained by melting this alloy with copper so that the correct percentage of aluminium is obtained (from 1·25 up to 10 per cent.).

The strength of current and horse-power of the dynamo used by the "Cowles Syndicate Co." have been already stated.

The amount of ferro-aluminium or aluminium bronze turned out daily is 750—1000 kg. (15—20 cwt.) containing 15 to 17 per cent. aluminium. The expenditure of energy necessary to produce 1 kg. of aluminium has been found to be on the average 50 h. p.[1] As it varies between 53·5 and 25, the lowest average that can be taken is 40 h. p.[1] The theoretical energy needed for 1 kg. of aluminium in bronze is only 8·87 h.p. Thus the waste of energy is very considerable. The reason appears to be that alumina is formed over again. The white smoke seen in the process seems to be newly formed alumina, formed by the reaction of aluminium vapour and carbon monoxide in the cooler part of the furnace.

---

[1] Borchers, *Elektrometallurgie*, p. 101.

At the Cowles Brothers' Works at Lockport in the State of New York, water-power to the extent of 1,200 h. p. is at their disposal; and from 2 to 3 tons of aluminium bronze are said to be daily produced. The walls of the vessel are lined with wood-charcoal, mixed with chalk, because otherwise the charcoal might be converted into graphite while the current passes, and graphite is a good conductor of heat and electricity.[2]

B. *Héroult's Process*

In this process alumina is not only fused by an electric current, but decomposed, and the aluminium alloyed with another metal at the moment it is set free. The second metal in molten condition forms the cathode, the anode is a bundle of carbon pencils. Alumina, fused by the current, forms the electrolyte. This process and its apparatus were described on p. 648.

The method was originally used, and is still, in improved form, at the works of the Aluminium-Industrie-Actien-Gesellschaft at Neuhausen in Switzerland. The power necessary to drive the dynamos is obtained from the falls of the Rhine, which work two turbines of 600 h. p., one of 300 h. p., and four older ones of 150 h. p. each. The two large ones have the electrodynamic machines above them on the same axis. This pair of machines give, with 150 turns to the minute, a current of 14,000 amp. with a potential of 30 volt. This is sufficient to reduce alumina. The dynamo which is worked by the 300 h. p. turbine is used to produce a magnetic field with 24 poles, and this supplies the lighting as well as working various other machines. The other turbines provide additional power when required.

With these arrangements three tons of aluminium bronze with 10 per cent. of aluminium can be produced daily.

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[1] Dammer, *Chem. Techn.*, vol. ii., p. 222.

[2] Dr. Charles v. Hahn. *Zeitschr. fur Elektrotechnik*, 1895, p. 479.

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THE END

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